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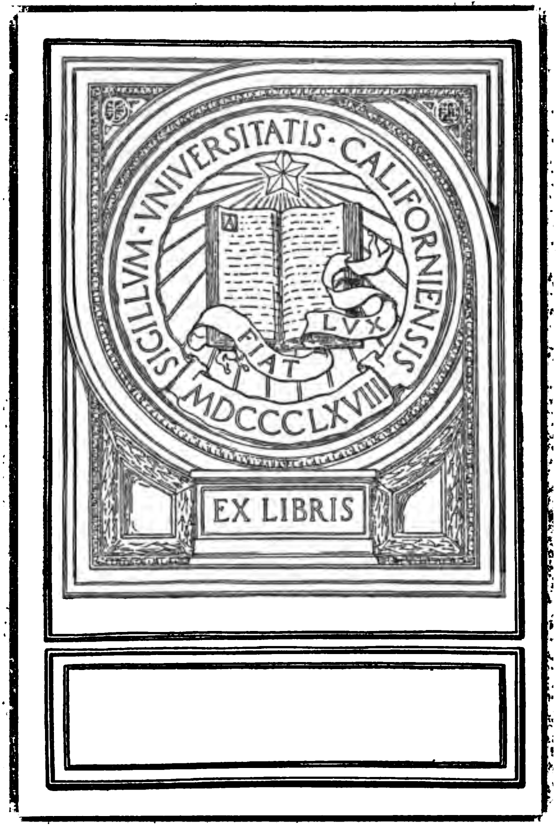
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CALIFORNIA

No. 2041

REPORT ON THE FIXATION AND UTILIZATION OF NITROGEN

PREPARED BY THE
NITRATE DIVISION, ORDNANCE OFFICE
U.S. WAR DEPARTMENT
ASSISTED BY THE
FIXED NITROGEN RESEARCH LABORATORY
DEPARTMENT OF AGRICULTURE

WASHINGTON
GOVERNMENT PRINTING OFFICE
1922

TP245
N3 U51

CERTIFICATE: By direction of the Secretary of War, the matter contained herein is published as administrative information and is required for the proper transaction of the public business.

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CALIFORNIA

LETTER OF TRANSMITTAL.

MARCH 29, 1922.

From: The Chief of Ordnance.
To: The Secretary of War.
Subject: Comprehensive Report on Nitrogen Fixation and Utilization.

1. In accordance with your instructions contained in the letter on "Policy on Nitrogen Fixation Activities" dated April 30, 1921, reference 670 (Miscl.) CHA*MC58, Ordnance file No. 111.3/1441, 5-2-21, a comprehensive report on the fixation and utilization of nitrogen has been prepared in the office of the Nitrate Division and is submitted herewith.

2. This report includes a discussion of the nitrogen situation of the world together with pertinent world statistics; a discussion of the history, chemistry, and construction and operating costs of the various nitrogen fixation processes; and a history and description of the United States Government nitrate plants.

3. It is believed the report will prove of great value to private citizens, schools and universities, and to the various Government departments, as well as to congressional committees and the individual members of Congress, and will answer the many questions eminating from these sources.

4. The printing of this report, which will make copies available for distribution through the office of the Superintendent of Documents, is being arranged.

C. C. WILLIAMS,
Major General, Chief of Ordnance.

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ACKNOWLEDGMENT.

This report was prepared in the Nitrate Division of the Ordnance Office, War Department, under the direction of Maj. J. H. Burns, by Capt. D. P. Gaillard, Mr. F. A. Ernst, Mr. P. E. Howard, Mr. A. E. Hecker, Mr. R. S. Tour, and Miss N. Churchill, of the Nitrate Division, and by Dr. R. C. Tolman, Dr. J. M. Braham, Dr. S. Karrer, Dr. Graham Edgar, Dr. A. T. Larson, Mr. E. W. Guernsey, Mr. H. J. Krase, and other members of the staff of the Fixed Nitrogen Research Laboratory of the Department of Agriculture.

In the preparation of this report extensive use was made of the many reports on file and the papers published by those associated with the Government's nitrate activities during the war, as well as of Government and private publications antedating the war.

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UNIV. OF CALIFORNIA

CHAPTER I.

INTRODUCTION.

A. PURPOSE.

This report has been prepared in order to correlate and make available under one cover such information on the fixation and utilization of nitrogen, collected by the Nitrate Division since its organization in July, 1917, as may aid in the further development of that art in the United States. It is based to a very considerable extent on reports, papers, and articles prepared by the officers and civilians associated from time to time with the activities of the Nitrate Division, as well as on the published technical and economic papers of several others. In order that it may be of further help to those who desire to make a more detailed study of any of the several phases of this subject, a bibliography of many of the papers pertaining thereto that have appeared in the last few years has been prepared and is included.

In this report there is first discussed the world's nitrogen supply and demand, including a brief discussion of the prices of nitrogen, then the development of nitrogen fixation both in this and in foreign countries, then a technical and engineering description of the several nitrogen fixation and conversion processes, a discussion of research in its bearing both on the present and future possibilities of fixation, a history of the Government's activities in nitrogen fixation, a description of the United States Government's nitrogen fixation plants, and the bibliography referred to above.

B. UTILIZATION OF NITROGEN.

1. For Military Explosives.

Almost without exception all military explosives are nitrogen compounds. Owing to the slight affinity between nitrogen and the other elements with which it enters into combination, many of its compounds are unstable and can be decomposed with the almost instantaneous evolution of heat and gas.

Black powder, the original military explosive, and practically the only one up to some 30 years ago, has as one of its three constituents a nitrogen compound, saltpeter. Since 1890, however, nitration processes have been developed until now practically all modern explosives are made by treating various bases with nitric acid; for instance, smokeless powder from cotton and nitric acid; nitroglycerin, the basis of dynamite, from glycerin and nitric acid; picric acid from carbolic acid and nitric acid; trinitrotoluene—T. N. T.—from toluol and nitric acid; fulminate of mercury from mercury and nitric acid; and ammonium nitrate from ammonia and nitric acid.

2. For Fertilizer.

For plant growth, too, nitrogen in a chemically combined form in the soil is essential. Originally land was fertilized by placing back on it the animal and vegetable refuse of the farm, but this material, though of excellent quality, is not usually of sufficient quantity. As chemical knowledge has developed, however, study has shown that these organic or animal and vegetable materials can be supplemented by inorganic or mineral materials. As a result, practically all complete commercial fertilizers now contain, besides some form of organic nitrogen, a very considerable quantity of inorganic nitrogen, as well as the phosphoric acid and potash, also necessary for plant growth.

The requirement of nitrogen for fertilizer, though usually considered as a peace-time requirement, is even more a war-time requirement, for while the population to be fed is practically the same, available labor for the farms is much reduced not only through enrollment in the Army but also through employment in munitions and war plants. The acreage under cultivation is therefore reduced, necessitating an increase in yield per acre. This can be accomplished by using in addition to all possible labor-saving farm machinery as much fertilizer and therefore as much nitrogen as possible.

3. For Industrial Purposes.

Nitrogen is also needed in many of the important chemical industries of the country. It is as necessary for commercial as for military explosives. Commercial explosives, such as dynamite, blasting powder, and the like, are used not only for practically all mining and quarrying operations but to a rapidly increasing extent for road building, clearing land, digging ditches, and in other operations as a means of saving labor.

Nitrogen as nitrate is necessary, too, for the comparatively new and rapidly developing nitrocellulose product industry which includes the manufacture of artificial leather, now almost universally used for automobile upholstery; of photographic films; of imitation ivory; and of all forms of celluloid. Nitrogen in this form is also needed for the manufacture of dyes, for the manufacture of sulphuric acid, and for the manufacture of a large part of our glass.

Nitrogen as ammonia is necessary for cold-storage plants and for the manufacture of artificial ice; it is found in nearly every home as household ammonia; and it is necessary for the production of several of the staple chemicals, including soda ash, which, next to sulphuric acid, is probably the most important commercial chemical. Cyanide is used in extracting gold from its ores and in insecticides.

C. SOURCES OF NITROGEN.

1. Organic Nitrogen.

The organic nitrogen from waste animal and vegetable materials is limited in amount and now can supply but a part of the fertilizer requirements. Almost no organic nitrogen goes into either military or other nonagricultural uses. The organic nitrogen materials include the animal and vegetable refuse of the farm, dried blood and tankage from the slaughterhouse, cottonseed meal from the oil mills, fish scrap, leather scrap, and similar materials. These were originally used almost entirely for fertilizers, but as many of them can be used to much better advantage as feed, they are being diverted more and more to that use, with the result that the present inadequate supply of these materials available for fertilizer is not only not keeping pace with the growth in the demand but is actually diminishing.

2. Inorganic Nitrogen.

The inorganic or mineral nitrogen comes from three sources, each of which now normally supplies about equal quantities of the world consumption. These, in the order of their development as sources of supply, are the natural nitrate beds of India and Chile, the by-product coke ovens, and the plants for fixing the nitrogen of the air.

a. Indian and Chilean nitrate.—For several centuries nitrate has been extracted from the soil of India and shipped as saltpeter to Europe and to this country. However, since their development, which began about 1830, the nitrate fields of Chile have been the world's chief source of supply of inorganic nitrogen, the production of India being insignificant in comparison. Even in spite of the tremendous development of the other two sources of inorganic nitrogen in the last few years, Chile still normally supplies about a third of the world's inorganic nitrogen requirements and nearly half of those of this country.

b. By-product coke ovens.—The next source of supply to assume importance was the by-product coke oven by means of which the nitrogen contained in bituminous coal is recovered when the coal is coked. The by-product coke oven as an important source of nitrogen supply is a more recent development than the utilization of the nitrate beds of Chile, and, even though to some extent outstripped in the last few years by the rapidly increasing number of plants for the fixation of atmospheric nitrogen, it now normally supplies about a third of the world's inorganic nitrogen requirements and nearly half of those of this country.

c. Nitrogen fixation plants.—The other important source of nitrogen supply, the one most recently developed and the one most rapidly growing, is the nitrogen fixation plant in which the nitrogen of the air is fixed in a usable form by means of one of several chemical and electrochemical processes. Although the first commercial nitrogen fixation plant started operating only 16 years ago, there are now some 40 plants located in 12 different countries, which together normally supply about a third of the world's nitrogen requirements. The United States has lagged behind in this development. Less than 2 per cent of our present normal requirements can be supplied from plants operating in this country, and even if the idle Government plant at Muscle Shoals were to be operated it would supply only an additional 19 per cent, still leaving us with only a fifth of our nitrogen from fixation plants. If to this we add the 7 per cent which can be supplied by the Canadian plant of an American company, we still lag behind the rest of the world, as all these plants can furnish only little more than a quarter of our requirements.

D. PRICES OF NITROGEN.

During the last few decades, in which the consumption of nitrogen has increased so tremendously, there has been no pronounced price trend either up or down. There have been marked variations from year to year, but the average price over a period of years has varied but little. It is believed that the reason for this has been the stabilizing effect of the elastic supply of Chilean nitrate, which in the past has set and still sets the price for the other sources of inorganic nitrogen.

The cost of nitrogen recovered as a by-product in the coke ovens is largely a matter of bookkeeping, and the coke ovens will make and sell their nitrogen for whatever it will bring, keeping their price low enough to insure a demand for their entire output. For this reason a country's requirements will first be supplied from this source. The requirements in excess of this supply will, generally speaking, be filled by the fixation plants as far as their capacity permits. Any deficiency in the supply still remaining will be met by importing sufficient Chilean nitrate. There are exceptions, of course, to this general rule, as certain uses require particular forms of nitrogen best supplied from one particular source, but, broadly speaking, Chilean nitrate supplies the last portion of the demand, and for this reason, in accordance with usual economic experience, it fixes the price for the other two sources.

The price of Chilean nitrate tends to stabilize itself over a period of years because of the flexibility of output. There has been no marked change in the last few decades in the cost of producing Chilean nitrate, since increased efficiency of operation has been offset by rising labor costs and by the fact that the richer deposits are becoming exhausted.

E. DEVELOPMENT OF NITROGEN FIXATION.

It was in 1898 that Sir William Crookes called attention to the fact that in a comparatively limited time the nitrate beds of Chile must inevitably become exhausted, and that a method must be developed for utilizing the vast store of nitrogen which constitutes four-fifths of the air, if the world is not to face ultimate starvation as a result of a deficiency of nitrogen fertilizers. This statement attracted world-wide attention and focused the interest of many on this problem. In fact, this date marks the beginning of industrial research on nitrogen fixation. It was not until some seven years later, however, that the first really commercial nitrogen fixation plants began operating.

1. Processes for Nitrogen Fixation.

At the present time there are many processes, differing greatly in principle, for fixing atmospheric nitrogen, and these processes are in various stages of development, ranging from those used in commercial plants which have been producing for years to those which have been tried only on little larger than a laboratory scale. There are four processes, however, which have been commercially utilized—the arc process, the cyanamide process, the synthetic ammonia process, and the cyanide process.

a. Arc process.—The first process to be utilized commercially was the arc process, still the simplest and most direct one.

In this process the nitrogen and the oxygen, both present in the air, are combined to form nitric oxide by being heated together to a high temperature by means of an electric arc. After quick cooling the gases contain a small percentage of nitric oxide, which on further cooling combines with additional oxygen of the air to form nitrogen dioxide. This nitrogen dioxide is then passed through large towers, over which water or weak acid is trickling, and combining with more oxygen from the air is absorbed by the water, forming dilute nitric acid.

There are several types of arc furnaces used, but these differ only in mechanical and electrical construction, the principle of all being very much the same.

It will be noted that the only raw materials used in this process are air and water. The power requirements, however, are so large, about 67,000 kilowatt hours per ton of nitrogen fixed, that this process can be used in its present state of development only where very cheap water power is available. For this reason this process has not been as extensively used as either the cyanamide or direct synthetic ammonia process. Its principal development has been in Scandinavia, although comparatively small-scale plants have been built in other countries. At present less than 10 per cent of the world's supply of nitrogen fixed from the air comes from plants using the arc process.

b. Cyanamide process.—The next process, the commercial development of which started almost at the same time as that of the arc process, is the cyanamide process.

In this process burned lime and coke are combined in the intense heat of the electric furnace to form calcium carbide. This carbide, after cooling, is finely ground, placed in closed ovens in an atmosphere of pure nitrogen, obtained by the fractional distillation of liquid air, and heated to a yellow heat. The nitrogen combines with the carbide to form calcium cyanamide. The crude calcium cyanamide is again finely ground and any carbide remaining destroyed by treating with water.

Details, especially of the equipment used in the several steps of the cyanamide process, differ considerably in the different plants throughout the world, but the essential principles are the same in all.

This process requires air, water, limestone, coke, and coal as its principal raw materials. Its electric power requirements, about 15,000 kilowatt hours per ton of nitrogen fixed, are so much less than those of the arc process that it is not nearly so dependent as that process on unusually cheap water power. Further, its intermediate product, the crude calcium cyanamide, is used to a considerable extent directly as a fertilizer material, even though there are limitations to its wider use. Two of its possible final products, ammonium sulphate and ammonium phosphate, are better fertilizer materials than those obtainable from the arc process.

For these reasons the cyanamide process is the most generally used of any of the fixation processes, there being more than 20 plants in 10 different countries, including the large Government plant at Muscle Shoals, Ala., now idle, and a smaller plant located in Canada but owned by an American company. At present under normal conditions somewhat more than a third of the world's fixed air nitrogen comes from plants using the cyanamide process. There is no cyanamide plant now operating in the United States, but practically all of the product of the Canadian plant is imported into this country, constituting about 7 per cent of our total inorganic nitrogen supply.

This process is now in an advanced state of development.

c. Direct synthetic ammonia process.—For some few years the arc and the cyanamide processes had the field to themselves. In 1913, however, the direct synthetic ammonia process developed by Doctor Haber was utilized on an industrial scale. In this process pure nitrogen and hydrogen, subjected to high pressure and high temperature, unite in the presence of a catalyst to form ammonia.

The nitrogen can be obtained from the fractional distillation of liquid air, and the hydrogen from the electrolytic decomposition of water. Ordinarily, however, this mixture of the two gases can be more cheaply prepared by the Bosch process utilizing a mixture of water-gas and producer-gas.

This process varies very considerably in the different plants in which it is used, the differences being principally in the method of preparing the nitrogen-hydrogen mixture and in the special catalyst and the pressure used for the ammonia synthesis.

The direct synthetic ammonia process requires air, water, and coke, as well as certain chemicals, as its raw materials. Its power requirements, provided the Bosch process is used for obtaining the nitrogen-hydrogen mixture, are much lower than even those of the cyanamide process, being only about 4,000 kilowatt hours per ton of nitrogen fixed. The engineering difficulties in safely handling these gases at high temperatures and pressures are very considerable, and in its present state of development a much more skilled personnel is required to operate this process than either the arc or the cyanamide processes.

The synthetic ammonia process has been developed almost entirely in Germany, and during the latter stages of the war was the most important source of her nitrogen supply. It was not until the present year, 1921, when at Syracuse, N. Y., the first plant of any size outside of Germany using this process, came into regular production. Though the Government had built a synthetic plant at Sheffield, Ala., during the war, it had not come into regular operation before the end of hostilities, when it was shut down. Experimental plants with only a very small production have been operated in France and Italy, and a commercial plant is now under construction in England. But the German plants up to this time have supplied all of the nitrogen fixed by this process, and their capacity is so great that in a normal year they furnish more than half of the world's supply of fixed air nitrogen. The plant at Syracuse, N. Y., has only about one one-hundredth of their capacity and can supply less than 2 per cent of the total inorganic nitrogen requirements of the United States.

d. Cyanide process.—The only other fixation process which has been used in full scale operation is the cyanide process, and this is as yet in a rather preliminary stage of development.

In this process soda ash, carbon, and iron are intimately mixed and heated to a red heat in the presence of nitrogen gas. The nitrogen combines with soda ash and carbon, forming sodium cyanide, the iron acting as a catalyzer.

The cyanide may be used in the metallurgical industry, as an insecticide, or it may be treated with steam to produce ammonia.

F. NITROGEN FIXATION ACTIVITIES OF UNITED STATES GOVERNMENT.

Although an American company had a cyanamide plant at Niagara Falls, Canada, which, in 1913, was probably the world's largest air nitrogen plant, the importance of nitrogen fixation both in its commercial and military aspects was thoroughly appreciated at that time by only a few in this country.

Developments early in the World War, however, showed the vital importance of Germany's nitrogen fixation plants in supplementing her inadequate supply of nitrogen from the by-product coke ovens and so enabled her to continue her production of military explosives with imports of nitrate from Chile cut off.

In 1915 the Chief of Ordnance in his annual report called attention to the absolute dependence of this country on Chile for an adequate war-time nitrogen supply. In 1916, as a result of this recommendation and the support received from the agriculturists who appreciated the value of an increased nitrogen supply for fertilizers, Congress appropriated $20,000,000 for the development by the Government of nitrogen fixation. After extended investigations by a committee of scientists and engineers, who recommended the use of the direct synthetic ammonia process developed by the General Chemical Co., the Ordnance Department in 1917 at Sheffield, Ala., started the construction of a plant to use this process, with an annual capacity of 8,000 tons of nitrogen.

The requirements for nitrogen, however, kept increasing as the war continued; there was danger that submarines might cut off, or seriously interfere with the Chilean nitrate supply; and the ships in the nitrate fleet were urgently needed to carry supplies overseas. As a result it was decided that additional nitrogen fixation capacity was needed. In view of the emergency it was considered best not to depend on the direct synthetic process, which though a success in Germany had never been used anywhere else, but to use the cyanamide process, which had been successfully operating in Canada for some six years. Late in 1917, therefore, at Muscle Shoals, Ala., using the processes of the American Cyanamid Co., construction was started on a plant with an annual capacity of 40,000 tons of nitrogen. Continually increasing requirements called for additional capacity and in 1918 plants each of half the size of the Muscle Shoals plant and almost identical with it were started at Cincinnati and Toledo, Ohio, and at the time of the armistice the necessity of still additional fixation plants was being very carefully considered.

A plant using the cyanide process, the products of which were to be used in chemical warfare, was also constructed at Saltville, Va., under the direction of the Bureau of Mines of the Interior Department. The Navy Department had also started late in 1918 the construction of a direct synthetic-ammonia plant at Indianhead, Md., which was to have the same capacity as the plant at Sheffield, Ala.

None of these plants had come into full production before the cessation of hostilities, when they were shut down. Trial operation had shown that the Sheffield plant needed further extensive modification of equipment and process before it could be depended upon to operate regularly; the Muscle Shoals plant had operated to the extent completed very successfully; the plant at Saltville had operated with some success from a technical point of view; the other cyanamid plants were each only about a third complete, and the Navy Department plant had just been started. In all some $107,000,000 had been spent during the war by the Government in connection with its nitrogen fixation program.

In order that the synthetic-ammonia process used in the Sheffield plant might be developed to a workable basis, the War Department undertook research on several phases of the process as well as engineering redesign of much of the equipment. Recent developments, however, by private industry apparently make unnecessary any further Government activities in connection with this process other than laboratory research, and justify the United States in depending entirely on private industry for the future industrial development of this process.

The case of the Muscle Shoals plant is somewhat different, for though the process is a well-developed one, on an entirely workable basis, the plant has sufficient production capacity to warrant its being kept in order that its production may be available in case of emergency. This means that it should either be retained and adequately maintained by the Government, or if disposed of, by sale or lease, to private industry there should be rigid guaranties as to its availability for nitrogen production in time of war.

Since the armistice governmental research on nitrogen fixation has been carried on largely at the Fixed Nitrogen Research Laboratory, originally organized in the Ordnance Department and recently transferred to the Department of Agriculture.

G. PRESENT STATUS OF NITROGEN FIXATION.

1. In the United States.

In this country there are the two commercial fixation plants, the synthetic-ammonia plant of the Atmospheric Nitrogen Corporation at Syracuse, N. Y., with an annual capacity of 3,000 tons of nitrogen, and the arc-process plant of the American Nitrogen Products Co., near Tacoma, Wash., with an annual capacity of some 300 tons of nitrogen. There are also the two Government fixation plants, now idle and in indefinite stand-by, the tried-out cyanamide plant at Muscle Shoals, Ala., with an annual capacity of 40,000 tons of nitrogen, and the synthetic-ammonia plant at Sheffield, Ala., which, with extensive modification of equipment, should have an annual capacity of 8,000 tons of nitrogen. There is thus an operating capacity of 3,300 tons and an idle capacity of an additional 48,000 tons. On the other hand, the present annual normal demand for inorganic nitrogen in this country over and above the 110,000 tons which can be furnished from the coking of coal is about 105,000 tons.

2. In Foreign Countries.

Our progress in nitrogen fixation shows up poorly in comparison with that of many other countries. Germany, besides having a by-product coke oven capacity somewhat greater than ours, possesses nitrogen fixation plants with an annual capacity of some 400,000 tons of nitrogen, giving her a total domestic supply more than sufficient for her needs, and rendering her entirely independent of imports. Great Britain, too, has about the same by-product coke oven capacity that we have, and, although she has no nitrogen fixation plant yet operating, there is one building, which it has been reported will have an ultimate capacity of 30,000 tons of nitrogen. Norway and Sweden, with their abundant cheap water power are well provided with fixation plants. Plants are also to be found in France, Switzerland, Italy, Holland, Austria, Japan, and Canada.

H. FUTURE OF NITROGEN FIXATION.

The nitrogen-fixation industry had such a forced growth during the war that its expansion in the immediate future will probably not be very great. Not only was this source of supply tremendously increased, but there was a considerable increase in the number of by-product coke ovens in many of the countries, including our own. With all this increased supply available, there has been a falling off in demand, due to the general world-wide economic conditions.

The result has been a marked depression in the nitrogen industry, and many fixation plants have been unable to stand the competition of the by-product coke ovens and of Chile and have been compelled to close down. But experience has shown that the world demand for nitrogen has doubled every 10 years, and it will be only a very few years until the demand catches up to the supply.

While the fixation industry is almost marking time, so far as expansion is concerned, it is far from marking time in research and development work. Existing processes and all their promising variants as well as entirely new processes are being carefully studied and tried out on small scale in an effort to get the process that can produce at lowest cost. This is taking place in all of the industrial countries of the world, and the United States is no exception.

CHAPTER II.

UTILIZATION AND SOURCES OF INORGANIC NITROGEN.

A. INTRODUCTION.

It has been truly stated that in the present state of civilization a nation lacking an adequate supply of nitrogen can be great neither in peace nor war. Nitrogen in its several combinations is an essential constituent of all fertilizers, it is needed in many of the basic industries, and it is absolutely necessary to the manufacture of practically all military explosives.

Experience has shown that the world's total consumption of nitrogen in the last few decades has doubled every 10 years, and the consumption in the United States has been increasing at an even more rapid rate. In order to get a true idea of the situation as to consumption and supply, it is equally as necessary to consider the trend of conditions from year to year as it is conditions as they are now. Therefore, past as well as present conditions will be included in the following discussion.

Both because more accurate information is available as to the situation in this country and because the situation here is not only fairly typical but it is of the greatest interest and importance to us, it will be considered first. In order, however, that this situation may be viewed in its proper perspective, and the possibilities of imports and exports considered, the world situation will then be discussed, though of necessity in less detail.

B. SITUATION IN THE UNITED STATES.

The domestic consumption of nitrogen, as has been stated, may be broadly divided into three parts: the agricultural, the industrial, and the military. The nitrogen exported must also be added in figuring our total nitrogen requirements.

To meet these requirements, there are two domestic sources of supply; first, the nitrogen recovered from the coking of coal either in by-product coke ovens or in gas retorts, and second, the nitrogen of the air transformed into usable form in the fixed nitrogen plants. The amount by which this domestic supply fails to meet the consumption must be made up by importing nitrogen either as nitrate of soda from Chile or as sulphate of ammonia or other nitrogen compounds from Europe.

The consumption of nitrogen in agriculture, in the industries, and for military purposes as well as for exports will first be considered, followed by a discussion of the supply from the coking of coal, from the nitrogen fixation plants, and from imports. Then will follow a brief discussion of nitrogen prices.

1. Nitrogen Consumed in Agriculture.

a. General.—Nitrogen, together with phosphorus and potassium, is essential to the growth of plant life. All fertilizers contain one or more of these elements, and most fertilizers contain all three. Of these, nitrogen is as important as any and, in the proportion ordinarily used, is the most expensive.

In the United States it is customary for the fertilizer manufacturer to mix, in various given proportions, materials containing these three elements, which are bagged and sold as mixed fertilizer to the farmer, some 60 per cent of the fertilizer used in this country being in the form of mixed goods.

The nitrogen in fertilizers is derived from two classes of materials—organic, or animal and vegetable materials, and inorganic, or mineral and so-called chemical materials. The most important organic materials are cottonseed meal and animal tankage, the latter a waste product of the meat-packing industry. Other organic materials used are garbage, fish scrap, hair, horns, scrap leather, and other such waste materials. The inorganic materials are nitrate of soda from Chile, sulphate of ammonia—the form in which nitrogen is usually recovered from the coke ovens, to a much less extent cyanamide—one of the forms in which nitrogen is fixed from the atmosphere, and a very small amount of other chemicals.

Statistics as to the quantities of each of these materials used for fertilizers are meager and conflicting. Perhaps the two most reliable sets of figures are those for 1913, as reported by the Federal Trade Commission, and those for 1917 and 1918, as reported by the fertilizer control of the Department of Agriculture. It so happens that the total fertilizer tonnage did not differ greatly in these three years. These figures, which include not only the nitrogenous materials used in the manufacture of mixed fertilizers but also those sold separately to the farmers, are shown in Table 1.

TABLE 1.—*Consumption of nitrogen in commercial fertilizers in the United States.*

	Per cent nitrogen in material.	Nitrogen contained in material (in net tons).				Average per cent of total nitrogen.
		1913	1917	1918	Average.	
Nitrate of soda	15.6	40,600	44,300	36,400	40,400	24.8
Ammonium sulphate	20.6	26,800	25,100	20,700	24,200	14.8
Cyanamide	18	2,800	6,700	1,100	3,500	2.2
Miscellaneous inorganic materials	....	....	2,200	800	1,000	0.6
Total inorganic nitrogen	....	70,200	78,200	59,000	69,100	42.4
Cottonseed meal	7	46,200	50,100	49,400	48,600	29.8
Tankage and blood	6-11½	26,000	27,600	20,100	24,600	15.1
Miscellaneous organic materials	6-15	16,500	22,200	23,300	20,700	12.7
Total organic nitrogen	....	88,700	99,900	92,800	93,900	57.6
Total nitrogen	....	158,900	178 200	151,800	163,000	100.0

Figures are approximate estimates, based, for 1913, on data contained in Federal Trade Commission "Report on the Fertilizer Industry," and for 1917 and 1918 on data in Department of Agriculture Bulletin 798, "A Survey of the Fertilizer Industry."

It will be noted that about three-sevenths of the total nitrogen was furnished by inorganic materials, Chilean nitrate supplying about three-fifths of this, sulphate of ammonia about a third, and cyanamide and miscellaneous materials the remainder. Of the organic nitrogen a little more than half was furnished by cottonseed meal, a little more than a quarter by tankage and blood, and the rest by the many miscellaneous organic materials. With two marked exceptions, in the case of nitrate of soda and of sulphate of ammonia, practically all of these materials go into mixed fertilizers. Somewhat more than a third of the nitrate and more than half of the cottonseed meal are sold direct to the farmers for separate application to the soil.

b. Growth in the use of fertilizers.—Commercial fertilizers first began to be used in this country about 50 years ago, and their use has increased steadily since that time. By 1899 the value of the fertilizers produced was more than seven times their value in 1869. From 1899 to 1914 the growth was at a much more rapid rate, as is shown in Table 2.

TABLE 2.—*Production of fertilizer in the United States.*

Year.	Total fertilizer.		Complete and ammoniated fertilizer.		Other fertilizer.	
	Net tons.	Value.	Net tons.	Value.	Net tons.	Value.
1899	2,887,114	$42,097,673	1,622,474	$28,781,883	1,264,640	$13,315,790
1904	3,591,771	56,928,034	2,385,201	44,325,882	1,206,570	12,602,152
1909	5,618,234	100,089,971	3,523,759	74,109,307	2,094,475	25,980,664
1914	8,432,206	153,260.212	5,612,421	121,676,386	2,819,785	31,583,828
1919	8,291.000	280,280,000	4,696.000	196,343,000	3,595,000	83,937,000

From U. S. Census statistics; figures for 1919 are preliminary.

It will be noted that in the 10 years prior to 1914 the use of commercial fertilizers more than doubled, the rate of growth in each 5-year period being substantially the same. In 1915, owing to the influence of the war, with the abnormally low price received for the cotton crop, the consumption of fertilizer decreased very considerably. There was a still further slight decrease in 1916, but since then and until the present year the consumption increased at approximately the rate that prevailed from 1909 to 1914. In the present year, however, the consumption has been abnormally low, due again to the abrupt fall in the price of farm products and particularly of cotton. There is little doubt, though, that in a year or two the use of fertilizers will again increase at a rapid rate.

Although the South has been and still is the principal user of fertilizer in the last few years, having taken nearly 65 per cent of the total production, the Middle West has shown the largest rate of growth from 1910 to 1914 and since 1916, and in 1920 used over 12 per cent of the total. In New England, which uses in the neighborhood of 5 per cent, and the Middle Atlantic States, which use about 17 per cent, the growth has not been so rapid. The figures from 1910 to 1920 are shown in Table 3:

TABLE 3.—*Fertilizer consumption in sections of United States.*

Year.	For Southern States.	For Middle Atlantic States.	For Middle Western States.	For New England States.	For other States and Porto Rico.	Total for United States.
	Net tons.	*Net tons.*	*Net tons.*	*Net tons.*	*Net tons.*	*Net tons.*
1910	3,978,372	1,003,500	426,041	274,300	71,342	5,753,555
1911	4,416,117	1,064,250	481,024	304,000	82,375	6,347,766
1912	4,140,779	1,105,466	458,221	323,000	84,550	6,112,016
1913	4,511,756	1,207,513	576,360	342,000	74,216	6,711,845
1914	5,107,244	1,301,139	634,500	391,500	83,145	7,517,528
1915	3,498,106	1,253,404	592,252	358,000	79,950	5,781,712
1916	3,463,407	1,137,255	521,007	368,000	93,380	5,583,049
1917	4,004,285	1,318,692	570,812	410,923	118,331	6,423,043
1918	4,426,586	1,305,132	726,168	433,000	100,857	6,991,743
1919	4,490,561	1,167,383	805,500	323,000	61,752	6,848,196
1920	5,123,098	1,247,273	930,132	341,450	58,636	7,700,589

Figures from The American Fertilizer Handbook.

c. Need for fertilizers.—This very rapid growth in the use of fertilizers in the United States is only repeating what has taken place in Europe. It was first felt in the South and the East. The use of fertilizer in the Middle West has already begun, however, and will inevitably increase faster in the future than in the past.

If the prices of nitrogenous fertilizers were low enough, there is for practical purposes almost no limit to the amount that could be advantageously used. It has been estimated by Doctor Lipman, director of the New Jersey Agricultural Experiment Station, that the annual loss of nitrogen from all land under cultivation in the United States which is not replaced by manure, by the nitrogen supplied by plowing under leguminous crops, by atmospheric precipitation in the form of rain and snow, and by the present use of commercial fertilizer, amounts to between 3,000,000 and 4,000,000 tons of nitrogen, to replace all of which would take from 15,000,000 to 20,000,000 tons of sulphate of ammonia, or from 150,000,000 to 200,000,000 tons of ordinary commercial mixed fertilizer.

Of course it would not pay now or in the immediate future to use fertilizer to any such extent on all of the land under cultivation, but these huge figures represent the upper limit to the use of nitrogen in fertilizer, and show how far from that limit the present consumption is.

d. Future use of fertilizer.—It will be more and more advantageous to use fertilizer in the future. The value of land in the agricultural sections of the country must inevitably increase and farm labor will become more and more difficult to get. The use of fertilizer which causes a greater production per unit of land and per unit of farm labor must inevitably increase, and, assuming that a sufficient supply is available, it is not unreasonable to predict that it will increase even faster in the future than it did before the war.

e. Increasing use of inorganic nitrogen in fertilizers.—Besides the steady and rapid increase that there has been, and which, it is believed, there will continue to be in the use of commercial fertilizers, there is another tendency in the fertilizer industry that has an important bearing on the requirements for inorganic nitrogen for fertilizer use. That tendency is the use of more inorganic and less organic nitrogen in fertilizer. This has come about not through the choice of either the manufacturers or users of fertilizer but because the supply of organic materials is a relatively inelastic one and can not respond to the increasing demands.

All of the organic nitrogenous materials are the by-products of other industries, principally the meat-packing and the cottonseed-oil industries; and though these industries have grown steadily during the last 20 years, their growth has not been nearly as rapid as the growth in the consumption of fertilizer. This is especially true of the meat-packing industry. Also, during this same period, there has been a steadily increasing use both of cottonseed meal and of blood and animal tankage for feeding purposes. The net result has been to make available for fertilizer use an amount of organic nitrogen slowly increasing up to a few years ago. Since then there has been, generally speaking, no increase but rather a fairly considerable decrease.

It is entirely logical that these materials should be used for feeds rather than for fertilizers. If used for feeds, they take the place of equivalent quantities of the more expensive feedstuffs, while, if used for fertilizers, they replace the less expensive inorganic nitrogenous materials—nitrate of soda or ammonium sulphate.

Figures compiled by the Department of Agriculture show that in 1917 and 1918 about half of the high-grade animal tankage and about two-thirds of the cottonseed meal was being used for feed, and it is believed that these proportions will undoubtedly increase. That these materials are now primarily feeds and only secondarily fertilizers is shown by the fact that their price is controlled more by the feedstuff market than by the prices of their competitive nitrogenous fertilizer materials, Chilean nitrate and ammonium sulphate.

Table 4 shows how the use of inorganic nitrogen in mixed fertilizers has been increasing during the last 20 years.

TABLE 4.—*Sources of nitrogen in mixed fertilizers in the United States.*

IN POUNDS OF MATERIAL PER NET TON OF "COMPLETE AND AMMONIATED" FERTILIZER.

Year.	Nitrate of soda.	Ammonium sulphate.	Cyanamide.	Cottonseed meal.	Tankage and other ammoniates.
1899	14.5	5.1	0	[1] 11.4	([2])
1904	28.2	8.9	0	[1] 92.6	([2])
1909	44.5	37.2	0	([2])	([2])
1914	52.4	53.4	9.2	115.9	316.3
1919	53.8	56.7	7.2	95.3	270.2

From United States census statistics; figures for 1919 are preliminary.

IN POUNDS OF NITROGEN PER NET TON OF "COMPLETE AND AMMONIATED" FERTILIZER.

Year.	Nitrate of soda.	Ammonium sulphate.	Cyanamide.	Total inorganic.	Cottonseed meal.	Tankage and other ammoniates.	Total organic.	Total.
1899	2.3	1.1	0	3.4	0.8	([2])	([2])	([2])
1904	4.4	1.8	0	6.2	6.5	([2])	([2])	([2])
1909	6.9	7.8	0	14.7	([2])	([2])	([2])	([2])
1914	8.2	11.0	1.7	20.9	8.1	20.6	28.7	49.6
1919	8.4	11.7	1.3	21.4	6.7	17.6	24.3	45.7

[1] Estimated from United States census figures for value of materials.

[2] Figures not available.

It will be noted how the quantity of inorganic nitrogen per ton of nitrogen containing fertilizer (a complete fertilizer contains nitrogen, phosphoric acid, and potash, and an ammoniated fertilizer nitrogen and phosphoric acid) has increased more than sixfold from 1899 to 1919. Unfortunately, figures are not available prior to 1914 as to the quantities of organic ammoniates, other than cottonseed meal, which were used. It is evident, however, that, unless the average nitrogen content of the nitrogen-containing fertilizers was in 1899 only 60 per cent what it was in 1919—and it is not believed that such was the case—the relative use of these organic materials must have decreased markedly. This conclusion is borne out, too, by the change shown in the figures from 1914 to 1919. The case of cottonseed meal is somewhat different. In the last 20 years there has been, broadly speaking, little increase in the cotton crop and therefore in the tonnage of seed available. The increasing proportion of seed crushed, however, has made a steadily increasing quantity of meal available. This increase was rapid enough for a time, even with the rapidly increasing use of meal as a feed, to furnish an increasing supply for fertilizers. This is shown by the marked increase in the figures from 1899 to 1914. Since 1914, however, the proportion of seed crushed has been approaching the limit, and the relative supply available for fertilizers has been decreasing, as shown by the change in the figures from 1914 to 1919.

Another marked change that has been taking place in the sources of nitrogen in mixed fertilizer is shown by the increasing proportion of the nitrogen furnished by ammonium sulphate, the use of which has increased even more rapidly than that of its competitive inorganic material—Chilean nitrate. It will be noted that in 1919 over ten times as much sulphate was used per ton of nitrogenous fertilizer as was used 20 years earlier, whereas the use of Chilean nitrate in this same period increased only threefold.

This growing appreciation of the value of sulphate in mixed fertilizers is very fortunate, for sulphate is primarily a domestic product, while all the nitrate is imported from Chile. As the by-product coke oven sulphate capacity in this country increased by some 80 per cent during the war, there is little doubt that the proportion of sulphate used in mixed fertilizers will continue to increase.

f. Summary.—In considering the consumption of inorganic nitrogen in fertilizers, two important tendencies should be kept clearly in mind: First, the rapidly increasing use of fertilizers; and, second, the marked change that is taking place in replacing the organic by the inorganic nitrogen materials. The net result is a consumption of inorganic nitrogen in fertilizers which has been increasing, and which will continue to increase, at a rate even more rapid than that in the use of fertilizers.

2. Nitrogen Consumed in Industries.

a. Uses of nitrogen in industry.—In the chemical industries, in which is included the manufacture of industrial explosives, nitrogen plays a very important part. This nitrogen is consumed in two forms, as nitric acid made from Chilean nitrate, and as ammonia furnished by the gas works and by the by-product coke ovens. At present about 60 per cent of the nitrogen is consumed in the form of nitrate and about 40 per cent in the form of ammonia.

Table 5 gives the consumption of the nitrate of soda.

TABLE 5.—*Consumption of nitrate of soda in the United States.*

Use.	1899		1904		1909		1914		1919	
	Net tons.	Per cent of total.	Net tons.	Per cent of total.	Net tons.	Per cent of total.	Net tons.	Per cent of total.	Net tons.	Per cent of total.
Explosives	88, 524	60.7	133, 034	60.4	188, 889	57.0	190, 960	46.2	174, 742	42.1
Chemicals and acid	37, 892	26.0	45, 021	20.4	52, 976	16.0	58, 101	14.1	85, 020	20.6
Other industries	....	......	....	......	....	......	1, 503	0.4	8, 428	2.0
Total industries	126, 416	86.7	178, 055	80.8	241, 865	73.0	250, 564	60.7	268, 190	64.7
Fertilizers	19, 518	13.3	42, 213	19.2	89, 846	27.0	162, 184	39.3	147, 558	35.3
Total reported	145, 934	100.0	220, 268	100.0	331, 711	100.0	412, 748	100.0	415, 748	100.0
Total United States imports	164, 071	......	255, 475	......	473, 192	......	606, 720	......	456, 410	......

From U. S. Census statistics; figures for 1919 are preliminary. Figures for imports from records of Bureau of Foreign and Domestic Commerce.

It will be noted that a very considerable portion of the nitrate of soda is not accounted for in the above tabulation. The discrepancy is most noticeable in the case of the 1914 figures, though the figures for 1919 are only apparently in better agreement, for, in addition to the nitrate imported in that year, there was at least a quarter as much again furnished by the surplus war stocks. The nitrate not accounted for in the tabulation was probably used, for the most part, for fertilizer sold directly to the farmer and therefore does not appear in the census returns of the fertilizer manufacturers. The figures for the industries, however, are somewhat lower than statistics collected during 1918 would have indicated probable, and it may well be that some of the unaccounted-for nitrate should be included there.

The figures do, however, give an idea of the relative amounts of nitrate used for the different purposes, and they show how the total consumption has increased in the last 20 years, for industries more than doubling, and for manufactured fertilizers increasing nearly eightfold in this period. It will be noted that about two-thirds of the nitrate used in the industries goes, after being converted into nitric acid, into the manufacture of industrial explosives, such as dynamite, blasting powder, etc., which are used not only for practically all mining and quarrying operations but to a rapidly increasing extent for road building, clearing land, digging ditches, and other operations. About a third of the industrial nitrate goes into the chemical industries, where it is used for the manufacture of nitric acid and to a lesser extent in the manufacture of sulphuric acid by the chamber process. A large part of this nitric acid is used in the rapidly growing nitrocellulose product industry, which includes artificial leather, now almost universally used for automobile upholstery, photographic films, imitation ivory, and all forms of celluloid. A relatively small amount, included in "other industries" in the tabulation, is used in the glass industry.

The figures for the consumption of ammonia, not including that of sulphate of ammonia, which is almost all used for fertilizer, are given in Table 6.

TABLE 6.—*Consumption of Ammonia in the United States.*

[Sulphate of ammonia not included.]

Use.	1899		1904		1909		1914		1919	
	Net tons.	Per cent of total.	Net tons.	Per cent of total.	Net tons.	Per cent of total.	Net tons.	Per cent of total.	Net tons.	Per cent of total.
Refrigeration	[1] 1,222	....	[1] 2,876	30.9	[1] 5,985	33.2	[1] 8,330	32.9	[1] 27,350	....
Chemicals	....	....	[2] 6,683	65.7	[2] 11,490	60.1	[2] 13,724	54.1	....	....
Explosives	[3] 54	....	[3] 316	3.4	[3] 1,200	6.7	[3] 3,288	13.0	[3] 4,737	....
Total	(4)	....	[5] 9,875	100.0	[5] 18,675	100.0	[5] 25,342	100.0	[5] 34,947	....

[1] From U. S. Census statistics; figures for 1919 are preliminary.
[2] Estimated, by differences.
[3] Estimated from U. S. Census figures for ammonium nitrate manufactured.
[4] No data available.
[5] From Table 10, this chapter.

The figures showing the ammonia used for refrigeration are the Census figures for anhydrous ammonia production and are probably quite accurate, although the figure for 1919 is surprisingly large and may include some ammonia used in the chemical industry. The figures for the ammonia used for explosives are probably also approximately correct, but those given for chemicals, which are figured by differences, can only be considered as indicative, as the figures for total production are from a different source and may not be strictly comparable. These figures for total production are obtained by adding to the figures for ammonia produced as such in the by-product coke ovens the entire output of the gas works. The relatively small part of the ammonia production from gas works which goes into the manufacture of sulphate may be assumed without serious error to balance that small part of the sulphate going into the chemical industry.

The tabulation, however, indicates the relative amounts of ammonia used for the different purposes. It will be noted that disregarding the incomplete 1919 figures, about a third of the ammonia consumed in the industries is used in the rapidly growing refrigeration industry, for the operation of cold-storage plants, and for the manufacture of artificial ice; that somewhat more than half of the ammonia is used in the quantity production of staple chemicals, principally soda ash, ammonium chloride, and sodium cyanide, and in the manufacture of household ammonia; and about one-eighth of the ammonia goes into the explosive industry for the manufacture of the ammonium nitrate used in "permissible" explosives.

b. Increase in consumption.—It will be noted that the threefold increase reported in the industrial consumption of nitrate of soda in the 20 years from 1899 to 1919 is less than the increase in imports during this period, which increased at nearly double this rate. On the other hand, the industrial consumption of ammonia, owing to the rapid increase of the refrigeration industry, and the growing consumption of ammonium nitrate in the manufacture of explosives, had a tenfold increase in this same period, an increase not much different from that in the total consumption of ammonia and its compounds for all purposes.

It is not probable that the consumption of nitrogen in the industries will continue to increase at such a rapid rate in the future, but it is believed that the actual average annual increase—not the percentage increase—will be even greater in the future than in the past.

In the preceding discussion it has been assumed that the requirements for nitrogen as nitrate and as ammonia are entirely distinct. The development during the war of the process for the oxidization of ammonia to nitric acid has shown that the conversion of ammonia nitrogen to nitrate nitrogen is entirely practicable, and should, in the future, ammonia be relatively much more plentiful than nitrate, and its price, therefore, enough lower to offset the expense of conversion, there is no doubt that a considerable part of the requirements for nitrate nitrogen would be supplied by the conversion of ammonia nitrogen.

3. Nitrogen Consumed in Military Explosives.

a. Past consumption.—Prior to the outbreak of the World War the total consumption of nitrogen in this country for military explosives increased from a few hundred tons in 1900 to between one and two thousand tons in 1914. Exact statistics on the consumption during this period are not readily obtainable, and, since the use of nitrogen for this purpose is such a very small part of the total consumption, exact figures are not necessary.

In the latter part of 1915 the manufacture of military explosives for the Allies began, and from that time on until the termination of hostilities in 1918 the production of military explosives in this country increased at a tremendous rate.

Table 7 shows the estimated quantity of nitrogen used in the manufacture of military explosives in 1918, the year of maximum consumption.

TABLE 7.—*Estimated consumption of nitrogen in 1918 in the United States for military explosives.*

Explosive.	Quantity produced for military use.	Nitrogen required.		
		As nitrate nitrogen.	As ammonia nitrogen.	Total.
	Net tons.	*Net tons.*	*Net tons.*	*Net tons.*
Ammonium nitrate	77,200	15,400	14,700	30,100
T. N. T	77,500	20,900	0	20,900
Picric acid	58,600	19,300	0	19,300
Other high explosives	25,700	9,500	500	10,000
Total high explosives	239,000	65,100	15,200	80,300
Smokeless powder	261,700	70,700	0	70,700
Total	500,700	135,800	15,200	151,000

Figures for high explosives are estimates based on data given in "American Production of Military High Explosives and Their Raw Materials," by Lieut. Commander Carleton H. Wright, U. S. Navy, U. S. Naval Institute Proceedings, October, 1920. Figure for production of smokeless powder is estimate based on records of Council of National Defense.

As has been stated, nitrogen can be converted through the oxidation of ammonia from its ammonia form to its nitrate form. This was actually done in 1918 in the two Government nitrate plants, which, however, were completed and came into production so late in the year that they furnished less than a thousand tons of the ammonium nitrate reported.

To furnish the 135,800 tons of nitrate nitrogen and the 15,200 tons of ammonia nitrogen required 870,000 tons of Chilean nitrate and 18,500 tons of ammonia, equivalent to 74,000 tons of sulphate of ammonia. This quantity of nitrate was greater than the total consumption in the United States for all purposes in any year prior to the World War.

In 1918, too, a military reserve stock of Chilean nitrate was gradually built up with the object of ultimately accumulating a sufficient quantity to last for six months should all imports be cut off. It was believed that a six months' stock, augmented by severe rationing of nitrogen for all nonmilitary uses, would be sufficient to last until additional fixation plants of sufficient capacity to meet the demand could be built and rushed into production. A smaller stock of ammonium sulphate, to be used in one of the processes for manufacturing ammonium nitrate, was also being accumulated. As a result of this accumlation, at the end of 1918 some 80,000 tons of nitrogen was on hand in these accumulatel stocks.

In other words, the accumulation of these essential reserves, together with the actual consumption in the manufacture of military explosives, required in 1918 in the neighborhood of 230,000 tons of nitrogen, equivalent to more than 1,474,000 tons of Chilean nitrate, a quantity of nitrogen more than a third greater than our consumption of inorganic nitrogen in all forms and for all purposes in any year before the World War. This military consumption of nitrate added to the nonmilitary consumption necessitated our importing from Chile almost three times as much nitrate as had ever been imported before the war. In June, 1918, for example, there were 105 steamers and 23 sailing vessels, aggregating some 700,000 tons, in the "nitrate fleet," and this at a time when we needed every ship for forwarding troops and supplies to France.

b. Future consumption.—The future consumption of nitrogen in military explosives, as long as the United States is not involved in war, will be but little larger than was the case before the war. In fact, for the next few years it will probably be less, as the large amounts of powder and expolsives now in storage, though requiring reworking from time to time, will require little additional consumption of nitrogen. In any event, the peace-time consumption of nitrogen for military explosives will be a negligible factor in the total consumption. As long, however, as the production of nitrogen in this country is inadequate to meet even our peace-time demands, and we are so largely dependent on imported nitrogen for our supply, conditions will be no different in case of a future war. In that event, the first effort to meet the situation would probably be an attempt to restrict the nonessential uses of nitrogen. Study and experience during the war both show, however, that very few of the uses are nonessential. Certainly refrigeration and fertilizers are even more necessary in war than in peace for insuring an adequate supply of foodstuffs. During a major war the only way to meet the condition of diminished labor supply on the farms, coupled with a demand for maximum production, is to increase the production per man by the use of fertilizer and to preserve the products by refrigeration.

The next effort undoubtedly would be to adapt the existing domestic sources of supply; that is, the by-product coke ovens and the nitrogen fixation plants, to produce nitrogen in the exact form needed for the manufacture of explosives. Fortunately, this is a matter involving few technical difficulties, and the time required for this would probably be no more than that needed to get into operation the explosives plants themselves.

Coincident with these efforts, assuming that we retained control of the seas, imports would be increased to the maximum extent. The question of shipping, which was so critical during the last war, would not be such a factor now, owing to the greatly increased American tonnage available; but it must be remembered that imports are absolutely dependent upon our maintaining uninterrupted a long sea line of communications.

In any event, it would almost certainly be necessary to duplicate the existing nitrogen fixation plants, and experience shows that this could not be done in very much less than a year, and only in that time by expanding a going organization familiar with the manufacturig processes.

In order that this country may be adequately prepared, it is necessary that there should be a military nitrogen reserve sufficient to last until additional facilities can get into production. The Ordnance Department of the Army now has such a reserve, consisting of loaded ammunition, bulk explosives, and a stock of Chilean nitrate, and is, further, maintaining the nitrate plant at Muscle Shoals in stand-by ready to start production in case of emergency.

c. Summary.—In the case of military explosives we have a negligible consumption in time of peace, increasing suddendly and enormously in case of war, when it becomes not only the most vital but the largest part of the total consumption. It is almost impossible to predict what this consumption would amount to in a future war, but it is safe to say that the future use of explosives in warfare will greatly surpass their use in this war, for as time goes on the real strength of an army is more and more dependent on its chemical munitions. Such has been the development in the past, and such will be the development in the future.

4. Nitrogen Exported.

In the past, and, in fact, until the last three years, but little inorganic nitrogen has been exported, as this country itself has been such a heavy importer. A large part of the little inorganic nitrogen exported was contained in mixed fertilizers manufactured here.

However, since the war, with the great reduction in the sulphate exports from Europe and the largely increased production of sulphate in the United States, our exports of sulphate of ammonia, largely to the West Indies and to the Far East, have become of sufficient magnitude to be of importance. Exports of nitrogen in other forms are still comparatively small in amount.

The exports of sulphate from the United States in recent years are shown in Table 8.

TABLE 8.—*Exports of sulphate of ammonia from the United States.*

	1916	1917	1918	1919	1920	1921
Sulphate of ammonia (net tons)...........	[1] 12,640	[1] 902	([2])	([3])	[4] 120,000	[5] 41,765

[1] From "Price of Fertilizers," War Industries Board Price Bulletin No. 48.
[2] Negligible.
[3] No data available.
[4] Estimate. Export figures of Bureau of Foreign and Domestic Commerce show exports of 66,714 tons, May to December, inclusive.
[5] For first eight months only.

It is unfortunate that more complete statistics are not available, but records have been kept of our exports only since May, 1920. There is no doubt, though, that in 1920 we exported more sulphate than we have ever imported in any past year.

At first it may seem peculiar that we were exporting sulphate and at the same time importing nitrate. The fact is, however, that sulphate is preferred to nitrate as a fertilizer for rice and sugar cane, the principal crops in those countries that took the bulk of our sulphate. On the other hand, in this country, nitrate of soda, the original inorganic fertilizer material, is still preferred by many as a fertilizer in spite of the increasing use of sulphate.

The question as to what may be expected in nitrogen exports from this country in the future is most uncertain, depending largely on whether we can meet the competition of the European sulphate. It is probable, however, that our exports will continue at an appreciable rate. It is very desirable that there be exports, both from a commercial and a military point of view, as exports not only help our foreign trade but also make available an additional source of supply in case of war.

5. Nitrogen Recovered From Coal.

a. General.—The first sources of nitrogen supply that will be considered, the sources that furnish practically all of the nitrogen produced in this country, are the by-product coke ovens and the coal-gas works. In these, when the coal is coked, a part of the nitrogen originally contained in it is recovered.

Bituminous coal, used for coke manufacture, contains from 1 to 2 per cent of combined nitrogen. During the coking process, from a fifth to an eighth of this nitrogen is given off in the form of ammonia, the rest escaping as free nitrogen or remaining in the residual coke only to escape later as free nitrogen when the coke is burned. The amount of nitrogen recovered varies with the character of coal used and the conditions under which the by-product coke ovens are operated. The ammonia gas, which constitutes only a very small portion of the coke-oven gases, is removed from the latter by absorption either in sulphuric acid to make ammonium sulphate or in water to make ammonia liquor. Ammonia is only one of the by-products obtained, the principal others being tar, light oil, and gas. In the simpler beehive ovens, still extensively used, only a form of tar is recovered, all of the gas from the coking process being allowed to escape without treatment.

By-product coke ovens were first introduced into this country about 1893, but by 1900 the coke production from this source was only 5 per cent of total. Table 9 shows how the by-product coke production has increased since 1900.

TABLE 9.—*Production of coke and pig iron in the United States.*

Year.	By-product coke.	Beehive coke.	Total coke.	Per cent by-product.	Pig iron.	Pounds of coke per pound of pig iron.
	Net tons.	*Net tons.*	*Net tons.*		*Gross tons.*	
1900	1,075,727	19,457,621	20,533,348	5.2	13,789,242	1.33
1901	1,200,000	20,600,000	21,800,000	5.5	15,878,354	1.23
1902	1,400,000	23,900,000	25,300,000	5.5	17,821,307	1.27
1903	2,000,000	23,300,000	25,300,000	7.9	18,009,252	1.25
1904	2,200,000	21,600,000	23,800,000	9.2	16,497,033	1.29
1905	3,462,348	28,768,781	32,231,129	10.7	22,992,380	1.25
1906	4,500,000	32,000,000	36,500,000	12.3	25,307,191	1.29
1907	5,400,000	35,100,000	40,500,000	13.3	25,781,361	1.40
1908	4,200,000	21,800,000	26,000,000	16.1	15,936,018	1.46
1909	6,300,000	33,000,000	39,300,000	16.0	25,795,471	1.36
1910	7,138,734	34,570,076	41,708,810	17.1	27,303,567	1.37
1911	7,847,845	27,703,644	35,551,489	22.1	23,649,547	1.34
1912	11,115,164	32,868,435	43,983,599	25.3	29,726,937	1.32
1913	12,714,700	33,584,830	46,299,530	27.5	30,966,152	1.34
1914	11,219,943	23,335,971	34,555,914	32.5	23,332,244	1.32
1915	14,072,895	27,508,255	41,581,150	33.8	29,916,213	1.24
1916	19,069,361	35,464,224	54,533,585	35.0	39,434,797	1.28
1917	22,439,280	33,167,548	55,606,828	40.4	38,621,216	1.29
1918	25,997,580	30,480,605	56,478,185	46.0	38,230,440	1.32
1919	25,143,542	19,043,000	44,186,542	56.9	30,508,122	1.29
1920	30,908,000	20,980,000	51,888,000	59.6	36,242,748	1.28
1921	[1] 13,107,154	[1] 3,821,000	[1] 16,928,154	77.5	[1] 11,236,466	1.34

[1] Figures for 1921 are estimated production for first eight months only.

All figures, except those for 1921, are from following publications of United States Geological Survey: For pig iron, for 1900–1917, from "Iron Ore, Pig Iron, and Steel in 1917"; for 1918–1920, from "Mineral Resources of United States." For coke, for 1900, 1901, 1905, and 1910–1917, from "Coke and By-products in 1916 and 1917"; for 1902–1904 and 1906–1909, from "Coke in 1915"; for 1918, from "Mineral Resources of United States"; and for 1919 and 1920, from Weekly Coal Reports.

These figures show a more or less constant growth in the production of by-product coke to 1912. The result of this very rapid growth was a tendency toward an oversupply of by-products, and consequently the building of additional by-product ovens was somewhat checked until stimulated again in 1915 by the demand for the by-products for the manufacture of munitions. In 1917 and 1918, in order to secure an adequate supply of toluol for the manufacture of T. N. T., the Ordnance Department of the Army by special contracts caused the construction of many additional ovens, the last of which were not completed until 1920. As a result of this increase the by-product ovens furnished nearly 60 per cent of all the coke produced in 1920, and in the first eight months of the present year, as a result of the business depression reducing the production of the beehive ovens much more than that of the by-product ovens, the proportion of by-product coke increased to more than three-quarters of the total.

This growth in the by-product coke production, it should be noted, had not, up to the last three years, been accompanied by any general decrease in the production of beehive coke. Production had varied from year to year, but the average production during the 15 years before 1919 had remained very nearly the same, with the by-product ovens supplying all the increase in the demand, but not to any great extent taking the place of the beehive ovens.

b. Future by-product coke production.—The demand for coke is to a very considerable extent determined by the condition of the iron industry, a fundamental industry of the country, which varies from year to year according to general business conditions. The preceding tabulation shows how closely the consumption of coke has followed the production of pig iron. This tabulation also shows that, although the iron industry has grown somewhat irregularly, periods of reduced production following every few years periods of record production, there has been a steady and constant increase in the average production.

At present there are considerable accumulated requirements for iron and steel, for example, in construction work which has been postponed; it is believed that certain industries, such as the automobile and farm tractor industries, will require increasing amounts of steel; further, steel will probably be used more and more in place of wood. On the other hand, it is unlikely that railroad requirements for steel—a very considerable part of the total requirements in previous years—will be so great as in the past. Further, the production of pig iron in this country has doubled in the last 15 years, an increase much greater than that in the population. It is evident that this per capita increase in the consumption of iron and steel can not continue. It therefore seems entirely reasonable to assume that the production of pig iron in this country in the next few years will continue to increase by the average prewar amount of about a million and a quarter tons a year.

This growth in the iron industry sets a fairly definite limit to the amount of coke that will be required in the future, for although attempts have been made to introduce coke as a domestic fuel, the consumption for this purpose is as yet a negligible part of the total consumption.

It is entirely possible that within the next few years by-product ovens will in years of normal business activity supply from two-thirds to three-quarters of the total coke production, but it is unlikely that they will displace beehive ovens to any greater extent than this. The iron industry has always been a business of ups and downs, and consequently the coke requirements have fluctuated from year to year. The preceding tabulation shows in the last 15 years four cases in which the production of coke has fallen off very considerably from the previous year, the percentage of decrease ranging from 36 per cent to 15 per cent of the production of the previous year and averaging for these four years 25 per cent. This year the decrease from last year will probably be at least 45 per cent. A by-product oven once built must continue in operation as long as possible, not only because it must carry much heavier fixed charges on capital invested than the cheaper beehive oven, but if shut down it must be partly reconstructed at considerable cost before being placed in operation again. On the other hand, the simpler beehive oven can be put into operation after an extensive period of idleness at comparatively small cost. Business considerations would therefore indicate that the maximum production to be expected from by-product ovens would be that production necessary to supply the minimum requirements; the difference between the minimum requirements and the maximum requirements—that is, the noncontinuous requirements—being taken care of by the cheaper and simpler beehive ovens. A study of the figures given in the preceding tabulation for coke production from these two sources for the past few years shows clearly how much less the by-product production fluctuates with the variable demand. For instance, in 1908 the production of beehive coke fell off 38 per cent from the previous year's figures, while the production of by-product coke decreased 22 per cent. In 1911 the production of beehive coke fell off 21 per cent, while the production of by-product coke increased slightly. In 1914 the production of beehive coke fell off 33 per cent and by-product only 12 per cent. In 1919 the beehive production fell of 44 per cent and the by-product only 4 per cent. In the first 8 months of the present year the beehive production, it is estimated, has fallen off some 70 per cent and the by-product only about 35 per cent.

It is not believed that in the next few years there will be any great number of new by-product coke ovens constructed. Cost of construction is still above the prewar cost, and the capacity for the production of by-products from the coke ovens now built is approximately three times that of the highest prewar year. It seems probable that the number of by-product coke ovens will increase rather gradually in the next few years, until probably not more than three-quarters of our normal coke supply will be furnished by by-product ovens. After this it is entirely possible that the percentage of by-product coke will continue to increase very gradually, but it is believed that it will be many years before beehive ovens are entirely displaced. On this assumption the growth in the production of by-product coke ovens in the next several years will be limited to some 15 per cent of the 1920 production, to which must be added some three-quarters of the amount by which the future coke consumption exceeds that in 1920. If this growth is distributed over several years, as is probable, it will be a very much less rapid growth than has occurred since 1914.

c. Nitrogen recovered in the manufacture of coal gas.—In the manufacture of coal gas, coal is coked in retorts differing somewhat from by-product coke ovens. The gas given off contains a part of the nitrogen in the coal as ammonia, and this ammonia is recovered in very much the same way as is done in the case of the by-product coke ovens. Nearly all of the ammonia recovered at the gas works is, however, in the form of ammonia liquor instead of as sulphate.

d. Production of sulphate of ammonia.—In statistics of ammonia production the ammonia is ordinarily reported as "sulphate equivalent," or the amount of sulphate that the ammonia is capable of making. As 4 tons of sulphate can be made from 1 ton of ammonia, the "sulphate equivalent" is four times as large as the actual production of ammonia as such. Table 10 gives the production of ammonia from the by-product coke ovens and from the gas works, all figures referring to "sulphate equivalent."

TABLE 10.—*Production of ammonia in the United States.*

(All figures are in net tons of "sulphate equivalent.")

Year.	From by-product coke ovens.			From gas works, assumed as liquor.	Total as liquor.	Grand total.	Per cent of total produced as sulphate.
	As sulphate.	As liquor.	Total.				
1902	[1] 5,638	[2] 9,367	15,005	[3] 20,000	[1] 29,367	35,005	16.1
1903	[1] 6,200	[2] 15,287	21,487	[3] 20,000	[1] 35,287	41,487	15.0
1904	[1] 14,113	[2] 17,500	31,613	[3] 22,000	[1] 39,500	53,613	26.3
1905	[1] 19,332	[2] 19,912	39,244	[3] 25,000	[1] 44,912	64,244	30.1
1906	[3] 20,000	[3] 25,000	45,000	[3] 30,000	55,000	75,000	26.7
1907	[1] 24,441	[2] 38,520	62,961	[4] 36,600	[1] 75,120	99,561	24.6
1908	[1] 22,047	[2] 27,932	49,979	[4] 33,300	[1] 61,232	83,279	26.5
1909	[3] 40,200	[3] 43,200	83,400	[4] 31,500	74,700	114,900	35.0
1910	[5] 35,124	[5] 46,044	81,168	[4] 30,000	76,044	111,168	31.6
1911	[5] 36,460	[5] 51,953	88,413	[4] 32,000	83,953	120,413	30.3
1912	[5] 47,613	[5] 59,947	107,560	[4] 35,000	94,947	142,560	33.4
1913	[5] 86,671	[5] 62,250	148,921	[4] 42,000	104,250	190,921	45.4
1914	[5] 85,382	[5] 57,867	143,249	[4] 43,500	101,367	186,749	45.7
1915	[5] 99,950	[5] 72,756	172,706	[6] 51,921	124,677	224,627	44.5
1916	[6] 135,916	[5] 99,349	235,265	[4] 53,000	152,349	288,265	47.1
1917	[5] 176,361	[6] 104,035	280,396	[6] 44,274	148,309	324,670	54.3
1918	[6] 218,194	[6] 130,460	348,654	[7] 29,674	160,134	378,328	57.7
1919	[8] 272,116	[8] 101,071	373,187	[9] 38,715	139,786	411,902	66.1
1920	[8] 337,500	[8] 130,000	467,500	[3] 40,000	170,000	507,500	66.5
1921	....	....	[10] 200,000	[10] 25,000	....	225,000	....

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[1] Figures from "Artificial Gas and By-products in 1915," U. S. Geological Survey.
[2] Estimated by difference.
[3] Estimate.
[4] Estimate of The Barrett Co., New York, in "The American Fertilizer Handbook, 1921."
[5] Figures from "Mineral Resources of United States," as quoted in "Tariff Information Survey, Ammonium Compounds."
[6] Figures from "Coke and By-products in 1916 and 1917," U. S. Geological Survey.
[7] Figure furnished by U. S. Geological Survey.
[8] Figures from "Weekly Coal Report," U. S. Geological Survey; those for 1920 are preliminary.
[9] Estimated from Census data.
[10] Estimated for first eight months only.

It will be noted from Table 10 how very rapid has been the increase in the total ammonia production of this country, an increase due almost entirely to the growth in the number of by-product coke ovens, for the output of ammonia from the gas works, which now furnish less than 10 per cent of the total production, has increased but little in the last 10 years.

In Table 10, owing to lack of data, all of the ammonia output from the gas works has been listed as ammonia liquor. While this is not strictly correct, it is believed that no serious error is introduced, as the proportion of gas-works ammonia recovered as sulphate is small.

The ammonia output of the bone-carbonizing works is also so small that it has been neglected in the tabulation.

It will be noticed how the proportion of sulphate produced has increased in the last 20 years from a sixth to two-thirds of the total ammonia production. This rapidly increasing quantity of sulphate has been for the greater part used in the fertilizer industry. The increase in the fertilizer consumption of sulphate, however, has not been quite as rapid as the increase in production would indicate, for in the last 20 years the United States has changed from a fairly heavy importer of sulphate to an equally heavy exporter.

6. Nitrogen From Fixation Plants.

a. *Commercial plants.*—Up to the present year there has been almost no quantity fixation of atmospheric nitrogen within the limits of the United States. For a few years a small arc process plant operated in North Carolina, and more recently another small arc process plant, that of the American Nitrogen Products Co., has been operating in the State of Washington. This plant, however, produced sodium nitrite, a chemical used in the dyestuff industry, for which a better price could be obtained than for nitrogen either in the form of nitrate of soda or sulphate of ammonia. Some other experimental and development installations have operated on a very small scale, but the aggregate supply from all these sources has been a negligible factor in the country's total supply of nitrogen. Within the last few months, however, the Atmospheric Nitrogen Corporation has brought into production at Syracuse, N. Y., a newly constructed fixation plant using the direct synthetic ammonia process. This plant has an annual capacity of some 3,000 tons of nitrogen in the form of anhydrous ammonia, the form in which ammonia is usually used in the refrigeration industry, and a form of nitrogen commanding a better price than nitrogen either as sulphate of ammonia or as nitrate of soda.

b. *Government plants.*—During the war United States Nitrate Plant No. 1, at Sheffield, Ala., using the General Chemical Co.'s direct synthetic ammonia process, and United States Nitrate Plant No. 2, at Muscle Shoals, Ala., using the cyanamide process, were practically completed.

Experimental operation was started at plant No. 1, but regular production was not secured, and considerable modification of the equipment and process would be necessary before regular production could be secured from this plant.

Plant No. 2 was tested and showed conclusively that it could produce fixed nitrogen at its rated capacity—approximately 40,000 tons per year—at reasonable cost. Altogether, No. 2 plant produced about 600 tons of nitrogen in 1918 and about 700 tons of nitrogen in 1919.

c. Future production from fixation plants.—If the Government plant at Muscle Shoals should be leased or sold, and be operated for the fixation of nitrogen, the domestic production of nitrogen in this country would be increased by 40,000 tons of nitrogen, equal to a little over 40 per cent of the present nitrogen capacity of the by-product coke ovens and gas works. In order, however, for the Muscle Shoals plant to operate profitably, it is necessary not only that comparatively cheap water power be available, but also that the rental or purchase price paid for the plant be considerably less than would be determined by the present cost of reproduction. In other words, though the operation of this particular plant would be profitable under the preceding conditions, it is very unlikely that any additional cyanamide plants will be constructed in this country in the next few years unless there is a considerable change in conditions.

It is probable that the two commercial nitrogen fixation plants already operating in this country, which supply the relatively high-priced markets for sodium nitrite and anhydrous ammonia, will continue to operate. It is entirely possible that the plant at Syracuse may be extended to supply a considerable part of the entire consumption of anhydrous ammonia in this country. Beyond that point, however, where the product of this plant would have to compete directly with the lower-priced sulphate of ammonia or nitrate of soda for fertilizer use, expansion is more doubtful. The direct synthetic ammonia process, it is true, has been able to compete successfully in Germany with Chilean nitrate, but a large part of the cost of the German plants must have been amortized during the war, and the rate of exchange has made the price of the Chilean nitrate in Germany abnormally high.

7. Nitrogen From Imports.

a. Imports in the past.—In the past 20 years more than three-quarters of the nitrogen consumed in this country has been imported, principally from Chile in the form of nitrate of soda, usually known as Chilean nitrate.

The only known deposits of natural nitrate of soda which are of commercial importance are those located in the rainless regions of northern Chile. Scattered small deposits of low-grade nitrate have been found in this country, especially in southern California and in several other places throughout the world, but none of these has yet proved commercially workable.

The principal deposits in Chile are found in the Province of Tarapaca, in the saltpeter or nitrate zone which embraces the extension comprehended between the Camarones River in south latitude 19° 11′

on the north and parallel 27° to the port of Caldera on the south, a distance of 450 miles. The deposits are at intervals from the coast varying from 15 miles in the north to 93 miles in the south, and are at an altitude of from 3,600 to 13,000 feet above the sea.

The saltpeter in these nitrate deposits is found mixed with other substances, in which common salt predominates, but including also clay, gravel, and sulphate of soda. There are four strata recognized in the fields, although the composition of each varies from location to location. The uppermost layer is called chuca, and consists of the surface accumulation of the ages; the second layer, which is firmer in consistency, thicker, and much harder to penetrate than the chuca, is the costra; below this is found the caliche, the real, natural deposit of nitrate of soda, which may be almost pure chemically, but which is considered commercially valuable if it runs above 30 per cent of the salt. The fourth layer is the stratum of bed rock called gova.

In extracting this caliche a cata or small shaft is sunk through the surface deposits and caliche to the gova, where a hole is scooped out, in which is placed a charge of powder or dynamite. The débris resulting from the explosion of this charge is divided into masses that may be used for building material or such indifferent work, while the caliche is collected by itself, placed in mule carts, and transported to the factory or oficina.

The caliche itself is a combination of nitrate of soda, varying from 14 to 75 per cent or more; sulphate of soda, sodium chloride, iodine salts, small proportions of potash, magnesium, and lime with insoluble matter.

Upon reaching the refinery the caliche is crushed and run into huge vats, where the nitrate is lixiviated or leached out with boiling water. The boiling usually continues from 20 to 24 hours, according to the quality of caliche treated. After boiling, the solution is concentrated and clarified and run into crystallizing tanks, where it is allowed to stand for several days. When sufficiently dry, the crystals are thrown upon the stock pile, where the sun and wind complete the process of drying.

The nitrate is finally put into sacks weighing 100 kilograms (about 221 pounds) and loaded into cars for shipment to the seaports.

For a few years before the World War considerable amounts of sulphate of ammonia were imported, for the most part from England, furnishing at a maximum somewhat less than one-fifth of the total nitrogen imported; but during the war England needed this nitrogen at home, and imports from this source fell to almost nothing. The plant of the American Cyanamid Co. at Niagara Falls, Canada, for the fixation of atmospheric nitrogen entered into production in 1910, and imports of cyanamide from this plant have steadily increased since that date, but they furnished only a very small fraction of the total nitrogen imported. The main reliance of this country, however, in the past has been the importation of Chilean nitrate, and the abnormal war demands were met almost entirely by expansion of this source of supply.

Table 11 shows the imports of nitrate of soda, of sulphate of ammonia, and of cyanamide.

TABLE 11.—*Imports of principal inorganic nitrogen materials into the United States.*

Calendar year.	Nitrate of soda (15.6 per cent nitrogen).	Sulphate of ammonia (20.6 per cent nitrogen).	Cyanamide (18 per cent nitrogen).
	Net tons.	*Net tons.*	*Net tons.*
1900	217,199	10,672	....
1901	221,720	11,908	....
1902	[1] 225,000	11,294	....
1903	[1] 256,000	9,406	....
1904	255,475	10,577	....
1905	359,778	5,005	....
1906	416,838	14,946	....
1907	408,363	27,910	....
1908	347,998	32,394	....
1909	473,192	42,914	....
1910	592,672	92,342	3,109
1911	610,263	95,764	6,048
1912	544,714	60,073	11,665
1913	700,965	65,444	30,016
1914	606,720	83,360	24,408
1915	864,862	36,366	33,648
1916	1,364,533	14,517	32,483
1917	1,728,398	8,141	52,940
1918	2,066,483	3,352	50,634
1919	456,410	2,636	69,576
1920	1,480,553	2,233	79,862
1921	[2] 353,117	[2] 2,614	[2] 7,504

[1] Approximation

[2] For first eight months only.

All figures from records of Bureau of Foreign and Domestic Commerce, except those for sulphate of ammonia for 1900–1908; these figures are given in American Fertilizer Handbook, 1921. for exports from Great Britain to the United States, and probably are some 10 per cent lower than our total imports from all countries.

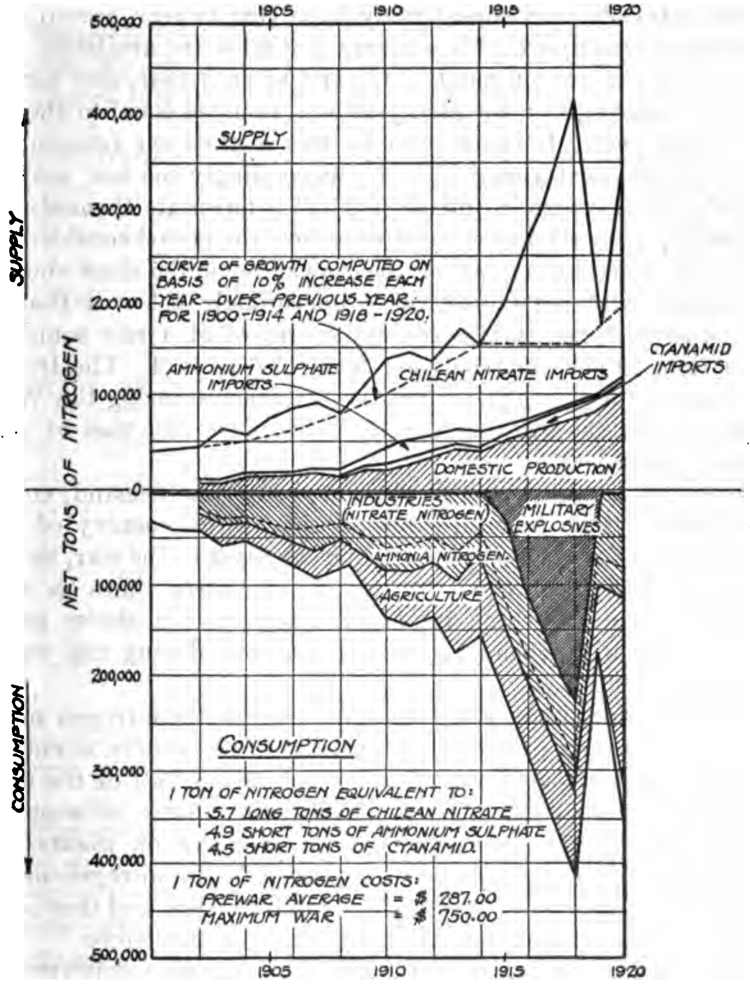
It will be noted how very much the imports of nitrogen in 1920 exceeded any previous peace-time year. These large imports, coupled with a record-breaking domestic nitrogen production and a lessened demand in the latter part of the year owing to business depression, resulted in such an oversupply of nitrogen and a carrying over of stocks at the end of the year that the imports during the present year, it will be noted, are even below the pre-war average and not so very different from those in 1919, when a similar situation prevailed.

The nitrogen materials listed in the tabulation—nitrate of soda, sulphate of ammonia, and cyanamide—are the principal inorganic nitrogen materials imported. Other materials imported which furnish any appreciable tonnage of nitrogen are muriate of ammonia or sal ammoniac, potassium nitrate, nitrate of lime, and ammonium nitrate. Imports of muriate of ammonia before the war averaged from 6,000 to 7,000 tons per year. Potassium nitrate imports averaged about 5,000 tons per year, with a maximum of 9,000 tons. Imports of nitrate of lime were stated in 1915 to amount to between 3,000 and 4,000 tons, nearly all of which went to the Pacific coast. Imports of ammonium nitrate were comparatively small before the war, increasing to some 2,000 tons in 1915 and to nearly 9,000 tons in the first six months of 1920. Other nitrogen materials imported, the quantity of which, however, was relatively negligible, were ammonium carbonate and other forms of ammonia and nitrate of soda. The nitrate of lime and probably most if not all of the ammonium nitrate are the products of the Scandinavian nitrogen fixation plants. The nitrogen in the muriate of ammonia comes from the coke ovens and gas works, and the nitrogen in the potassium nitrate is derived from the natural nitrate beds either of India or of Chile.

b. Imports in the future.—Consideration of the nitrogen situation indicates that the requirements of the country will in the future as in the past first absorb the domestic production, because domestic nitrogen can always undersell imported nitrogen. This is true with the nitrogen from the by-product coke ovens and gas works, where the cost of production, as is the case with any by-product, is largely a matter of bookkeeping. This also will be true if the Government nitrate plants are operated, as their operation would almost certainly not be undertaken unless it could meet the competition of imported nitrogen. The same thing, of course, applies to whatever nitrogen is produced in the future in privately owned fixation plants, for this source of supply will certainly not materialize unless private capital is convinced that nitrogen from this source can undersell, if necessary, any imported nitrogen. In other words, under the conditions that may be expected to prevail in the future, when the consumption will be considerably greater than the domestic supply, the price will be controlled by the cost of the imported nitrogen necessary to supply the deficiency in the domestic production, and the imports will therefore just be sufficient to meet whatever deficiency there may be.

Whether most of this imported nitrogen will be in the form of Chilean nitrate or whether some nitrogen may be obtained either from the European by-product coke ovens or from European fixation plants is immaterial. It is believed, however, that most of the imported nitrogen over and above the relatively small amount contained in the cyanamide imported from Canada will be furnished by Chilean nitrate, as has been the case in the past.

c. Summary.—In order that the conditions that have prevailed in the last 20 years in regard to the consumption and supply of nitrogen may be better realized and that the steady increase in consumption may be appreciated a chart (fig. 1) has been prepared.



CONSUMPTION AND SUPPLY OF INORGANIC NITROGEN IN UNITED STATES 1900–1920

CONSUMPTION IN EACH YEAR TAKEN EQUAL TO NET SUPPLY FOR THAT YEAR AS DATA LACKING FOR STOCKS ON HAND AT END OF YEAR.

FIGURE 1

Statistics that have already been given as to the total supply of nitrogen available in this country during each of the past 20 years are quite complete. There is not available, however, equally accurate information as to how this nitrogen was consumed, but an estimate believed to be fairly accurate was made for each year. The stocks of nitrogenous materials carried over from one year to be used in the next naturally vary considerably from year to year, according to the business conditions. No accurate statistics are available, however, as to the stocks on hand at the end of each year, and for this reason the consumption for each year was assumed equal to the supply for that year. If in one year by this method the consumption is too high, the next year will be correspondingly too low, and any relatively small errors so introduced will compensate themselves in studying the general trend of conditions over the period considered.

It will be noted by comparing the upper line on the chart showing total supply with the dotted curve immediately below it that the total use of nitrogen in this country increased at a rate somewhat greater than 10 per cent each year from 1900 to 1914. The tremendous demand for nitrogen for military explosives during the World War materially checked this growth in the peace-time uses of nitrogen from 1914 to 1919.

It will also be noted on this chart how the war demand, considerably greater than the entire consumption in this country of inorganic nitrogen for all purposes in any year prior to the war, necessitated importing from Chile in 1918 almost three times as much nitrogen as had ever been imported before, and it shows graphically how greatly dependent this country was during the war on this importation.

The chart shows further how the expansion of the nitrogen supply from coke oven and gas works, even though abnormally stimulated by war demand, can at present furnish only about half of the nitrogen requirements of the country. Unless this source of supply is supplemented by the production of nitrogen-fixation plants it is believed that in the next decade less than half the nitrogen needed in this country in time of peace will be produced here and that conditions, instead of becoming better, will slowly become worse.

This takes into consideration only the peace-time consumption. If in the next decade this country should become involved in another war taxing our resources to anything like the extent that they were during the World War, we would be only about 25 per cent self-sustaining in our nitrogen supply. Although during the World War we were supplying and preparing to supply to a not inconsiderable extent the ammunition requirements of our allies, as well as our own, in a future war with only our own requirements to take care of it is probable that the use of explosives would be increased over that in the World War enough to make our total requirements fully as great as they were at that time.

8. Prices of Inorganic Nitrogen.

The wholesale prices of inorganic nitrogen, nitrates, and ammoniates used for fertilizer show rather frequent and very sharp fluctuations, as may be noted in Table 12, which follows. This table shows the average wholesale prices each year for sulphate of ammonia since 1900, for nitrate of soda since 1906, and for cyanamide from 1913 through 1918.

TABLE 12.—*Average yearly prices (wholesale) for principal inorganic nitrogen materials.*

Year.	Price of material.			Price per ton of nitrogen in material.		
	Nitrate of soda per 100 pounds.	Sulphate of ammonia per 100 pounds.	Cyanamide per unit of ammonia.	In nitrate of soda (15.6 per cent nitrogen).	In sulphate of ammonia (20.6 per cent nitrogen).	In cyanamide (18 per cent nitrogen).
1900	(1)	$2.87	....	....	$279.00	....
1901	(1)	2.76	....	....	268.00	....
1902	(1)	2.98	....	....	289.00	....
1903	(1)	3.12	....	....	303.00	....
1904	(1)	3.11	....	....	302.00	....
1905	(1)	3.12	....	....	303.00	....
1906	$2.36	3.10	....	$303.00	301.00	....
1907	2.45	2.96	....	314.00	287.00	....
1908	2.27	2.95	....	291.00	286.00	....
1909	2.14	2.80	....	274.00	272.00	....
1910	2.12	2.64	(1)	272.00	256.00	....
1911	2.15	2.85	(1)	276.00	277.00	....
1912	2.44	2.99	(1)	313.00	290.00	....
1913	2.32	2.92	$2.17	298.00	283.00	$264.00
1914	2.12	2.69	2.15	272.00	261.00	261.00
1915	2.33	3.25	2.06	299.00	315.00	250.00
1916	3.18	3.78	2.08	480.00	367.00	253.00
1917	4.05	5.87	2.88	519.00	570.00	350.00
1918	4.68	6.71	3.21	600.00	651.00	390.00
1919	3.61	4.56	(1)	463.00	443.00	....
1920	3.52	6.15	(1)	451.00	597.00	....
1921	[2]2.54	[2]2.41	(1)	326.00	234.00	....

[1] Data not readily available.

[2] For first nine months only.

Figures for sulphate of ammonia for 1900–1906 are from Coal Gas Residuals, by Fred H. Wagner.

Figures for nitrate of soda for 1906–1912 and for sulphate of ammonia for 1907–1912 are from Federal Trade Commission Report on Fertilizer Industry, and are, respectively, prices in New York and at plants.

Figures for all materials for 1913–1918 are from War Industries Board Price Bulletin No. 48, Prices of Fertilizers, and are New York prices for nitrate and sulphate and Niagara Falls prices for cyanamide.

Figures for 1919–1921 are from Oil, Paint and Drug Reporter, and are, for nitrate of soda price in New York, and for sulphate of ammonia price at plants except when in 1919 and 1920 there were no price quotations at plants and export prices were used.

It will be noted that the average pre-war prices of sulphate and nitrate, allowing for the difference in nitrogen content, are very nearly the same; the average from 1906 to 1913 for sulphate being $281 and for nitrate $293 per ton of nitrogen content. The price of the nitrogen contained in cyanamide is lower, as that material is not as suitable for fertilizer use as is either of the others, and therefore must sell at a lower price to compete with them. The cost of cyanamide manufacture is discussed in Chapter IV of this report, and will therefore not be taken up here.

Practically all of the sulphate of ammonia produced is a by-product of the coke and gas industries, and can be sold therefore at actual cost of production; that is, cost of the sulphuric acid used plus actual manufacturing expense. The sale price is, however, fundamentally based upon the price of nitrate of soda and finally upon the law of supply and demand.

Nitrate of soda, on the other hand, is mined as such and must be sold at a price in excess of its cost on board ship, which includes production cost plus export duty.

This cost is distributed approximately as follows:

	Per cent.
Export duty	41
Supplies (sacks, oil, fodder, powder, etc.)	6
Freight, lighterage, and commission	11
Administration and general expenses	3
Labor	19
Coal	11
Amortization	9

The export duty, which was fixed by the Chilean Government at $11.39 pr short ton in 1880, has not been changed since that time.

The average cost of nitrate of soda per 100 pounds loaded on shipboard in the various ports of Chile in 1903, according to the Federal Trade Commission, was as follows:

Cost of mining	$0.25
Cost of refining	.16
General expenses	.04
	.45
Profits from company stores	.02
	.43
Sacks, cord, sacking, and loading	.04
Railroad freight	.09
Port expenses	.02
Export tax	.56
Commissions	.02
Total cost per 100 pounds alongside vessel	1.16

Since that time the cost has slowly but steadily increased to $1.51 per hundred pounds in 1908 and $1.67 in 1914, which is the cost at the present time, September, 1921. This increase in the cost of mining and refining nitrate has been due mainly to the marked advance in wages and in the cost of fuel.

Freight from Chile to the United States, which had risen from the pre-war figure of $7.50 per ton to $17.50 in 1919, is now below the pre-war rate.

It is believed that even in the face of severe competition this cost at ship side in Chilean ports could not be materially reduced for any length of time. Labor, due to the closing down of the copper mines and the cessation of work on railroad building, is plentiful, and the rate of pay, therefore, is at a low level and apt to increase rather than decrease, as the other projects mentioned have been only temporarily discontinued. The export duty levied by the Chilean Government can not be materially reduced, as this is that Government's main source of revenue and practically only means of support. The substitution of oil for coal as fuel has effected a reduction in fuel costs in the few oficinas in which it has been made from 25 to 40 per cent, and could result in a corresponding saving and reduction in costs in the other factories.

Fluctuations in the price of nitrate of soda at the various points of consumption did not cause corresponding fluctuations in price on the coast of Chile. The price has rather been fixed in the European market where its consumption for agricultural purposes was the heaviest. The very high prices for sugar in the world's markets in 1911 led to heavy sowing of sugar beets in Europe in 1912, with a greatly increased use of nitrate of soda for fertilizer. Stocks on hand were thereby depleted, causing the increase in price, as shown in the preceding table. In 1909, due to reports of European scientists that the nitrate deposits would soon be exhausted, the price of nitrate of soda went sharply upward in the European markets. This did not affect the markets of the rest of the world, however.

Although there have been temporary artificial influences, such as speculation and manipulation, which have sometimes affected the price of nitrate of soda and sulphate of ammonia, the price fluctuations have been governed fundamentally by the law of supply and demand.

It will be noticed how closely the prices of sulphate of ammonia and nitrate of soda have followed each other. An advance in the price of one material will usually lead to the substitution of the other, increasing the demand and causing a subsequent increase in price of this substitute.

This interrelation of the nitrates and ammoniates is, therefore, a very important factor in regulating prices.

It usually happens that sulphate of ammonia varies in price first, to be followed somewhat later by nitrate of soda. Several factors tend to make this so, viz, the present world production in tons of sulphate is considerably less than that of the nitrate, so that when the normal demand is satisfied there is less surplus sulphate to be disposed of; a much larger proportion of sulphate than of nitrate is used for fertilizer; the production of sulphate is not as responsive to the fluctuations of prices as is the production of nitrate of soda, since sulphate is a by-product of industries unrelated to agriculture or the needs for fertilizer, the total output each year depending to a considerable extent upon conditions in the coke and gas and the iron and steel industries.

C. WORLD NITROGEN SITUATION.

The world nitrogen situation in detail is shown in the following tables, which need very little explanation:

1. World Production of By-Product Ammonia.

Table 13 shows by countries the world production of by-product ammonia in net tons of sulphate equivalent. The greater part of the by-product ammonia is produced in the form of sulphate of ammonia, only a small portion being produced as aqua, ammonia liquor, and anhydrous ammonia.

TABLE 13.—*World production of by-product ammonia.*

(All figures are in net tons of "sulphate equivalent.")

Country.	1910	1911	1912	1913	1914
United States [1]	111,168	120,413	142,560	190,921	186,749
United Kingdom	415,000	[2] 431,973	[2] 434,905	484,532	477,581
Germany	[3] 417,760	[3] 468,160	[2] 551,040	605,163	456,173
France	[3] 64,176	[3] 70,000	[3] 76,720	82,121	[4] 70,000
Japan	[5] 1,230	[5] 4,248	[5] 8,030	8,818	17,675
Canada	[4] 7,000	[3] 7,124	[3] 11,289	10,607	8,571
Italy	[5] 7,889	[5] 9,574	[5] 12,224	14,802	15,789
Australia	[5] 3,857	[5] 3,064	[5] 3,300	6,048	6,328
Netherlands	[5] 5,830	[5] 6,600	[5] 7,700	7,716	5,512
Spain	[5] 9,900	[5] 13,200	[5] 13,200	16,535	17,637
Russia	....	[5] 569	[5] 4,400	15,222	18,983
Austria-Hungary	[5] 31,482	[5] 33,363	36,234	38,580	38,580
Total	1,075,292	1,168,288	1,301,602	1,481,065	1,319,528

Country.	1915	1916	1917	1918	1919	1920
United States [1]	224,627	288,265	324,670	378,328	411,902	507,500
United Kingdom	477,419	485,747	513,651	484,457	445,214	....
Germany	[3] 603,900	[4] 700,000	[3] 770,000	[4] 800,970	....	[4] 533,980
France	46,297	27,557	37,478	33,069	[5] 49,587	....
Japan	35,080	42,111	[3] 55,880	[5] 100,767	....	....
Canada	10,448	[3] 11,040	[4] 12,000	....	....	....
Italy	16,203	16,535	9,921	11,023	....	....
Australia	7,168	7,952	[5] 10,987	[5] 13,200	....	....
Netherlands	5,512	4,409	[4] 4,000	....	....	....
Spain	18,188	19,841	14,054	....	....	....
Russia	18,056	36,111	....	....	....	....
Austria-Hungary	38,580	38,580	38,580	....	....	....
Total	1,501,478	1,678,148	1,791,221	1,850,000	1,500,000	1,900,000

[1] Figures from Table 10.
[2] The American Fertilizer Handbook, 1921.
[3] Nitrogen Products Committee, Final Report (British Report).
[4] Estimated.
[5] International Institute of Agriculture, Rome, Italy.

All figures except otherwise noted from "Tariff Information Surveys," U. S. Tariff Commission. Figures not shown not available.

A falling off in production in 1914 will be noticed. Immediately following the declaration of war in Europe the steel markets of the world slumped, due to the impossibility of predicting the turn of events. This caused a curtailment in the production of coke. The slump was only temporary, however, and before the end of the year the demand for steel for shell and other materials of war had started the steel mills of the world to capacity production with preparations for expansion.

The production of by-product ammonia in France, it will be noticed, shows a falling off rather than increase during the war period. Almost from the first the occupation of French territory by German troops took place, with the consequent destruction of the numerous steel mills located in this territory, causing over a 50 per cent reduction in the iron and steel production capacity of France.

2. World Consumption of Nitrate of Soda.

Table 14 shows the world consumption of nitrate of soda by countries.

TABLE 14.—*World consumption of nitrate of soda.*

[In net tons.]

	1910	1911	1912	1913	1914
Total Europe	1,927,671	1,934,968	2,196,833	2,072,000	[1] 1,841,932
Germany	865,894	819,094	1,004,803	917,927	[1] 648,840
France	372,019	373,188	390,608	360,501	[2] 326,898
Belgium	316,933	334,706	341,357	350,941	[2] 173,422
Holland	153,310	159,378	199,343	181,249	[2] 86,547
England and Scotland	139,884	146,464	151,404	141,648	[2] 393,009
Italy	50,433	59,074	49,080	56,952	[2] 65,638
Austria-Hungary	6,519	5,818	7,838	8,203	....
Spain	12,071	9,891	14,934	14,489	[2] 39,670
Total United States	577,725	625,974	485,947	649,168	581,100
All other countries	95,608	84,920	105,493	96,114	86,600
Total	2,601,004	2,645,862	2,788,278	2,817,282	2,123,700

	1915	1916	1917	1918	1919	1920
Total Europe	1,111,700	1,651,400	1,168,400	956,650	508,250	1,454,400
Germany	....	....	....	....	....	....
France	[3] 277,057	[3] 581,908	[3] 491,079	[3] 281,745	[3] 171,194	....
Belgium	0	0	0	0	[3] 87,196	....
Holland	[3] 42,519	[3] 64,805	[3] 61,338	[3] 1,241	[3] 166,431	....
England and Scotland	[3] 405,822	[3] 456,163	[3] 271,990	[3] 588,170	[3] 27,485	....
Italy	[3] 78,903	[3] 94,214	[3] 114,565	[3] 106,713	[3] 14,151	....
Austria-Hungary	....	....	....	....	....	....
Spain	[3] 42,213	[3] 49,204	[3] 57,556	[3] 20,626	[3] 64,053	....
Total United States	909,250	1,300,200	1,672,250	2,100,600	353,300	1,385,700
All other countries	196,150	314,000	201,250	138,550	146,200	218,400
Total	2,217,100	3,265,600	3,041,900	3,195,800	1,007,750	3,058,500

[1] Figures for only six months' German consumption available.
[2] Final Report of Nitrogen Products Committee (British report).
[3] Data compiled by Statistics Branch, General Staff, U. S. Army.

Figures 1910-1913 from Federal Trade Commission Report on Fertilizer Industry.
Figures 1914-1920, except as otherwise noted, from International Institute of Agriculture, Rome, Italy.
Figures not given not available.

Immediately at the start of the war a blockade was effected which cut Germany off from importation of Chilean nitrate. At the same time, and continuing during the latter half of 1914, a German fleet stationed off the coast of Chile successfully prevented nitrate carriers bound for countries at war with Germany, and in many cases, those bound for neutral countries as well, from sailing. These conditions caused the drop in nitrate of soda consumption as noted for the years 1914 and 1915.

It will be further noted that the year 1919 shows a decided drop due to labor difficulties in Chile and shortage of coal, as well as to the cessation of the war demand and liquidation of war stocks. The consumption in the United States during the war period, 1917 and 1918, is also worthy of note. The importations during this period for the United States reached three-quarters of the pre-war requirements of the whole world and more than three times the British war demand.

No figures are available for the amount of nitrate, if any, which reached Germany during the war, but it is stated that very large stocks were captured at Antwerp in 1915.

3. Production and Consumption of Nitrogen.

Table 15, consisting of seven separate tabulations, shows the production and consumption of nitrogen in each of the principal consuming countries—Germany, United States, Great Britain, France, Japan, Italy, and Norway.

TABLE 15.

(Net tons of nitrogen.)

PRODUCTION AND CONSUMPTION OF NITROGEN IN GERMANY.

	1910	1911	1912	1913	1914	1915	1916	1917	1918	1919	1920
Domestic production:											
By-product ammonia	[1] 86,050	[1] 96,441	[1] 113,514	[1] 124,664	[1] 93,972	[1] 124,403	[1] 144,200	[1] 158,620	[2] 165,000	....	[2] 110,000
Fixed atmospheric nitrogen	[3] 4,108	[3] 4,455	[3] 4,356	[3] 11,550	[3] 20,724	[3] 132,990	[3] 166,980	[3] 233,300	[4] 324,610	....	[3] 393,000
Total production	90,167	100,896	117,870	136,214	114,696	257,393	311,180	391,920	489,610	....	503,000
Exports:											
Chilean nitrate [5]	[4] 4,112	[4] 4,018	[4] 4,279	[4] 4,299	[4] 4,011	0	0	0	0	....	....
By-product ammonia	[4] 16,570	[4] 16,889	[4] 12,999	[4] 17,222	[4] 16,962	0	0	0	0	....	....
Fixed atmospheric nitrogen	0	0	[4] 1,700	[4] 6,366	[4] 4,690	0	0	0	0	....	....
Total exports	20,682	20,907	18,978	27,887	25,663	0	0	0	0	....	....
Imports:											
Chilean nitrate	[4] 128,990	[4] 125,567	[4] 139,817	[4] 133,179	[4] 101,355	0	0	0	0	....	....
By-product ammonia	[4] 6,901	[4] 5,553	[4] 5,243	[4] 7,860	[4] 5,114	0	0	0	0	....	....
Fixed atmospheric nitrogen	0	0	[4] 6,380	[4] 11,191	[4] 4,438	0	0	0	0	....	....
Total imports	135,891	131,120	151,440	152,230	110,907	0	0	0	0	....	....
Total consumption	205,376	211,109	250,332	260,557	199,940	257,393	311,180	391,920	489,610	....	....

[1] From Table 13.
[2] Estimate.
[3] Nitrogen products committee, final report, London (1920.)
[4] International Institute of Agriculture, Rome, Italy.
[5] Reexports.

Figures not shown not available.

TABLE 15—Continued.

(Net tons of nitrogen.)

PRODUCTION AND CONSUMPTION OF NITROGEN IN UNITED STATES.

	1910	1911	1912	1913	1914	1915	1916	1917	1918	1919	1920
Domestic production:											
By-product ammonia	[1] 22,901	[1] 24,805	[1] 29,367	[1] 39,330	[1] 38,470	[1] 46,273	[1] 59,383	[1] 66,882	[1] 77,936	[1] 84,852	[1] 104,545
Fixed atmospheric nitrogen	0	0	0	0	0	0	0	300	300	300	300
Total production	22,901	24,805	29,367	39,330	38,470	46,273	59,383	67,182	78,236	85,152	104,845
Exports:											
Chilean nitrate[5]					[4] 1,607	[4] 3,965	[4] 9,337	[4] 12,166	[4] 8,516	[4] 2,128	
By-product ammonia	[4] 119	[4] 0	[4] 37	[4] 0	[4] 60	[4] 276	[4] 104	[4] 50	[4] 0	[4] 3,640	[4] 24,720
Fixed atmospheric nitrogen											
Total exports	119	0	37	0	1,667	4,241	9,441	12,216	8,516	5,768	24,720
Imports:											
Chilean nitrate	[4] 92,457	[4] 95,201	[4] 84,975	[4] 109,351	[4] 94,648	[4] 134,918	[4] 212,867	[4] 269,630	[4] 322,371	[4] 71,200	[4] 230,966
By-product ammonia	[6] 19,022	[6] 19,727	[6] 12,375	[6] 13,481	[6] 17,172	[6] 7,491	[6] 2,991	[6] 1,677	[6] 691	[6] 543	[6] 460
Fixed atmospheric nitrogen	[4] 560	[4] 1,089	[4] 2,100	[4] 5,403	[4] 4,393	[4] 6,057	[4] 5,847	[4] 9,529	[4] 9,114	[4] 12,524	[4] 14,375
Total imports	112,039	116,017	99,450	128,235	116,213	148,466	221,705	280,836	332,176	84,267	245,801
Total consumption	134,821	140,822	128,780	167,565	153,016	190,498	271,647	335,802	401,896	163,651	325,926

Figures except as noted taken from previous tables this report.

PRODUCTION AND CONSUMPTION OF NITROGEN IN GREAT BRITAIN.

	1910	1911	1912	1913	1914	1915	1916	1917	1918	1919	1920
Domestic production:											
By-product ammonia	[1] 85,490	[1] 88,986	[1] 89,590	[1] 99,814	[1] 98,382	[1] 98,348	[1] 100,064	[1] 105,812	[1] 99,798	[1] 91,714	
Fixed atmospheric nitrogen	0	0	0	0	0	0	0	0	0	0	
Total production	85,490	88,986	89,590	99,814	98,382	98,348	100,064	105,812	99,798	91,714	

Exports:											
Chilean nitrate [5]	[4] 1,244	[4] 1,469	[4] 2,424	[4] 1,859	[4] 3,369	[4] 9,340	[4] 127	[4] 846	[4] 0	[4] 0	....
By-product ammonia	[4] 65,412	67,151	[4] 65,743	[4] 74,510	[4] 72,270	[4] 67,775	[4] 59,808	[4] 14,515	[4] 4,417	[4] 21,780	....
Fixed atmospheric nitrogen	0	0	0	0	0	0	0	0	0	0	....
Total exports	66,656	68,620	68,167	76,369	75,639	77,115	59,935	15,361	4,417	21,780	....
Imports:											
Chilean nitrate	[6] 22,107	[6] 22,454	[6] 21,597	[6] 24,628	[6] 61,599	[6] 72,850	[6] 71,515	[6] 43,408	[6] 92,050	[6] 4,279	[6] 17,485
By-product ammonia	[4] 0	[4] 0	[4] 0	[4] 0	[4] 0	[4] 0	[4] 0	[4] 0	[4] 0	[4] 0	....
Fixed atmospheric nitrogen	[4] 2,610	[4] 3,944	[4] 3,725	[4] 5,958	[4] 8,206	[4] 16,895	[4] 22,115	[4] 21,861	[4] 13,487	[4] 7,536	....
Total imports	24,717	26,398	25,322	30,586	69,805	89,745	93,630	65,269	105,537	11,815	....
Total consumption	43,551	46,764	46,745	54,031	92,548	110,978	133,759	155,720	200,918	81,749	....

PRODUCTION AND CONSUMPTION OF NITROGEN IN FRANCE.

Domestic production:											
By-product ammonia	[1] 13,220	[1] 14,420	[1] 15,804	[1] 16,917	[1] 12,360	[1] 9,537	[1] 5,677	[1] 7,720	[1] 6,812	[4] 10,215	....
Fixed atmospheric nitrogen	[4] 198	[4] 297	[4] 990	[4] 1,485	[4] 1,485	[4] 15,840	[4] 19,800	[4] 19,800	[4] 19,800	0	....
Total production	13,418	14,717	16,794	18,402	13,845	25,377	25,477	27,520	26,612	10,215	....
Exports:											
Chilean nitrate [5]	[4] 807	[4] 631	[4] 1,756	[4] 904	[4] 358	[4] 368	[4] 2,028	[4] 1,243	[4] 76	[4] 93	....
By-product ammonia	[4] 190	[4] 292	[4] 449	[4] 261	[4] 301	[4] 399	[4] 335	[4] 303	[4] 19	[4] 46	....
Fixed atmospheric nitrogen	[4] 110	[4] 140	[4] 130	[4] 138	[4] 62	[4] 11	[4] 909	[4] 1,052	0	[4] 2	....
Total exports	1,107	1,063	2,335	1,303	721	778	3,272	2,598	95	141	....
Imports:											
Chilean nitrate	[4] 59,367	[4] 54,649	[4] 60,849	[4] 55,404	[4] 51,115	[4] 43,689	[4] 93,001	[4] 78,030	[4] 44,130	[4] 26,861	....
By-product ammonia	[4] 5,937	[4] 4,959	[4] 5,196	[4] 5,198	[4] 2,058	[4] 2,296	[4] 4,823	[4] 3,087	[4] 1,663	[4] 4,701	....
Fixed atmospheric nitrogen	[4] 85	[4] 275	[4] 521	[4] 1,652	[4] 629	[4] 406	[4] 1,318	[4] 1,523	[4] 1,418	[4] 1,054	....
Total imports	65,389	59,883	66,566	62,254	53,802	46,391	99,142	82,640	47,211	32,616	....
Total consumption	77,700	73,537	81,025	79,353	66,926	70,990	121,347	107,562	73,728	42,690	....

[1] From Table 13.
[4] International Institute of Agriculture, Rome, Italy.
[5] Reexports.
[6] American Fertilizer Handbook, 1921.

Figures not shown not available.

TABLE 15—Continued.

(Net tons of nitrogen.)

PRODUCTION AND CONSUMPTION OF NITROGEN IN JAPAN.

	1910	1911	1912	1913	1914	1915	1916	1917	1918	1919	1920
Domestic production:											
By-product ammonia	[1]253	[1]875	[1]1,654	[1]1,816	[1]3,641	[1]7,226	[1]8,675	[1]11,511	[4]20,758	....	....
Fixed atmospheric nitrogen	[4]0	[4]455	[4]1,040	[4]1,386	[4]1,485	[4]4,752	[4]4,752	[3]6,000	[3]9,000	....	....
Total production	253	1,330	2,694	3,202	5,126	11,978	13,427	17,511	29,758	....	....
Exports:											
Chilean nitrate[5]	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	....
By-product ammonia	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	....	....
Fixed atmospheric nitrogen	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	....	....
Total exports	0	0	0	0	0	0	0	0	0	0	....
Imports:											
Chilean nitrate	[4]2,422	[4]4,856	[4]3,302	[4]4,597	[4]4,201	[4]5,196	[4]7,916	[4]9,475	[4]8,412	[4]11,301	....
By-product ammonia	[4]15,764	[4]16,853	[4]19,204	[4]25,315	[4]23,978	[4]4,528	[4]1,626	[4]3,428	[4]247	[4]22,980	....
Fixed atmospheric nitrogen	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	[4]0	....	....	....
Total imports	18,186	21,709	22,506	29,912	28,179	9,724	9,542	12,903	8,659	34,281	....
Total consumption	18,439	23,039	25,200	33,114	33,305	21,702	22,969	30,414	38,417	....	....

PRODUCTION AND CONSUMPTION OF NITROGEN IN ITALY.

	1910	1911	1912	1913	1914	1915	1916	1917	1918	1919	1920
Domestic production:											
By-product ammonia	[1]1,625	[1]1,972	[1]2,518	[1]3,049	[1]3,253	[1]3,338	[1]3,406	[1]2,044	[1]2,271	....	....
Fixed atmospheric nitrogen	[4]638	[4]767	[4]1,768	[4]2,966	[4]3,080	[4]5,008	[4]4,981	[4]3,960	[3]4,000	....	....
Total production	2,263	2,739	4,286	6,015	6,333	8,346	8,387	6,004	6,271	....	....

Exports:											
Chilean nitrate[5]	[4] 17	[4] 29	[4] 5	[4] 11	[4] 31	0	0	0	0	0	....
By-product ammonia	0	0	0	0	0	0	0	0	0	0	....
Fixed atmospheric nitrogen	0	0	0	0	0	0	0	0	0	0	....
Total exports	17	29	5	11	31	0	0	0	0	0	....
Imports:											
Chilean nitrate	[4] 10,525	[4] 10,244	[4] 9,397	[4] 11,596	[4] 10,294	[4] 12,338	[4] 14,732	[4] 17,914	[4] 16,686	[4] 2,213	....
By-product ammonia	[4] 4,710	[4] 4,613	[4] 4,810	[4] 4,919	[4] 2,976	[4] 1,725	[4] 641	[4] 76	[4] 559	[4] 1,107	....
Fixed atmospheric nitrogen	0	0	0	0	0	0	0	0	0	0	....
Total imports	15,235	14,857	14,207	16,515	13,270	14,063	15,373	17,990	17,245	3,320	....
Total consumption	17,481	17,567	18,488	22,519	19,572	22,409	23,760	23,994	23,516	....	....

PRODUCTION AND CONSUMPTION OF NITROGEN IN NORWAY.

Domestic production:											
By-product ammonia	0	0	0	0	0	0	0	0	0	0	0
Fixed atmospheric nitrogen	[4] 3,511	[4] 5,516	[4] 11,993	[4] 18,092	[4] 18,004	[4] 19,820	[4] 33,972	[4] 46,818	[4] 50,654	[4] 50,620	....
Total production	3,511	5,516	11,993	18,092	18,004	19,820	33,972	46,818	50,654	50,620	....
Exports:											
Chilean nitrate[5]	0	0	0	0	0	0	0	0	0	0	0
By-product ammonia	[4] 91	[4] 54	[4] 39	[4] 31	[4] 64	[4] 37	[4] 0	[4] 11	0	0	....
Fixed atmospheric nitrogen	[4] 2,782	[4] 5,116	[4] 11,665	[4] 17,751	[4] 17,680	[4] 19,703	[4] 29,032	[3] 32,099	[3] 25,951	[3] 15,603	[3] 34,817
Total exports	2,873	5,170	11,704	17,782	17,744	19,740	29,032	32,110	25,951	15,603	....
Imports:											
Chilean nitrate	[4] 44	[4] 252	[4] 194	[4] 230	[4] 96	[4] 6	[4] 1,105	[4] 8	[4] 1	0	....
By-product ammonia	[4] 430	[4] 696	[4] 1,007	[4] 2,043	[4] 2,281	[4] 2,698	[4] 1,717	[4] 4,123	[4] 609	....	....
Fixed atmospheric nitrogen	0	0	0	0	0	0	0	0	0	0	....
Total imports	474	948	1,201	2,273	2,377	2,704	2,822	4,131	610	....	....
Total consumption	1,112	1,294	1,490	2,583	2,637	2,784	7,762	18,839	25,313	....	....

[1] From Table 13.
[2] Estimate.
[3] Nitrogen products committee, final report, London (1920).
[4] International Institute of Agriculture, Rome, Italy.
[5] Reexports.

Figures not shown not available.

The increase in production in fixed atmospheric nitrogen in Germany in 1913 marks the starting up of the Haber plant at Oppau, while that in 1915 marks the material expansion of this plant. Germany's second Haber plant, located at Merseburg, was placed into production in 1917 and 1918, resulting in the production increases as shown.

While cyanamide production was on the increase in Germany, its growth in comparison to the growth of nitrogen production by the Haber process was slow.

It will also be noted that whereas immediately prior to the war Germany produced 18 per cent of the world's fixed atmospheric nitrogen, in 1918, the last year of the war, she produced 72 per cent.

In the United States the vast increase in imports of Chilean nitrate was the principal source for supplying the increased demand for nitrogen. The increase in the number of by-product coke ovens, however, was responsible for more than doubling by-product ammonia production and for producing about one-fifth of the total nitrogen consumed. The Government's fixed atmospheric nitrogen plants did not get into operation in time to add to the nitrogen supply, and the only fixed atmospheric nitrogen produced was in the form of sodium nitrite produced by the small arc plant of the American Nitrogen Products Co., at Seattle, Wash.

Great Britain's sources of nitrogen were domestic production of by-product ammonia and importation of Chilean nitrate and fixed atmospheric nitrogen. The fixed atmospheric nitrogen was imported from Norway chiefly in the form of nitrate of lime for the manufacture of ammonium nitrate by double decomposition with ammonium sulphate. Toward the end of the war, however, this process began to be displaced by other methods, employing Chilean nitrate instead of nitrate of lime, accounting for the drop in imports of fixed atmospheric nitrogen noted for the years 1917 and 1918.

The consumption of nitrogen in France does not show the steady increase noted in connection with the other countries at war. In the first place, the increase in production of fixed atmospheric nitrogen scarcely more than equaled the decrease in by-product ammonia previously mentioned, and secondly, importations with the years 1916 and 1917 excepted were below pre-war figures. This condition was caused chiefly by lack of carriers.

A decrease in Japan in nitrogen consumption during the first years of the war will be noted. This was due to her inability to import sulphate of ammonia, a condition which was later overcome by the building of additional by-product coke ovens and cyanamide plants.

Italy shows but a very slight increase in consumption, her increase in domestic production of fixed atmospheric nitrogen being offset by her decrease in imports of sulphate of ammonia.

The striking feature in Norway's chart is the large increase in home consumption starting with the year 1917, when Norwegian nitrate of lime came into wide use as a fertilizer. It is to be noted that in the year 1918 ten times as much nitrogen was consumed as during pre-war years. It will also be noted that the fixed atmospheric nitrogen industry, which is almost evenly divided between the arc and the cyanamid processes, enjoyed quite an even rate of growth.

4. Summary of Production and Consumption of Nitrogen by Countries.

The production and consumption of nitrogen by countries as shown in Table 16 is rather an assemblage of the data of the previous tables in such form as to afford easy comparison.

TABLE 16.—*Production and consumption of nitrogen, by countries.*

[In net tons of nitrogen.]

Country.	1910		1911		1912	
	Consumption.	Production.	Consumption.	Production.	Consumption.	Production.
Germany	205,376	90,167	211,109	100,896	250,332	117,870
United States	134,821	22,901	140,822	24,805	128,780	29,367
Great Britain	43,551	85,490	46,764	88,986	46,745	89,590
France	77,700	13,418	73,537	14,717	81,025	16,794
Japan	18,439	253	23,039	1,330	25,200	2,694
Italy	17,481	2,263	17,567	2,739	18,488	4,286
Norway	1,112	3,511	1,294	5,516	1,490	11,993
All others	139,584	436,508	157,581	453,475	183,819	472,967
Total	637,324	654,511	671,713	692,464	735,829	745,561

Country.	1913		1914		1915		1916	
	Consumption.	Production.	Consumption.	Production.	Consumption.	Production.	Consumption.	Production.
Germany	260,557	136,214	199,940	114,696	257,393	257,393	311,180	311,180
United States	167,565	39,330	153,016	38,470	190,498	46,273	271,647	59,383
Great Britain	54,031	99,814	92,548	98,382	110,978	98,348	133,759	100,064
France	79,353	18,402	66,926	13,845	70,990	25,377	121,347	25,477
Japan	33,114	3,202	33,305	5,126	21,702	11,978	22,969	13,427
Italy	22,519	6,015	19,572	6,333	22,409	8,346	23,760	8,387
Norway	2,583	18,092	2,637	18,004	2,784	19,820	7,762	33,972
All others	188,309	502,372	115,807	470,725	96,744	364,629	156,816	575,870
Total	808,031	823,441	683,751	765,581	773,498	832,164	1,049,240	1,127,760

Country.	1917		1918		1919		1920	
	Consumption.	Production.	Consumption.	Production.	Consumption.	Production.	Consumption.	Production.
Germany	391,920	391,920	489,610	489,610	....	....	....	....
United States	335,802	67,182	401,896	78,236	163,651	85,152	325,923	104,845
Great Britain	155,720	105,812	200,918	99,798	81,749	91,714	....	....
France	107,562	27,520	73,728	26,612	42,690	10,215	....	....
Japan	30,414	17,511	38,417	29,758	....	....	....	....
Italy	23,994	6,004	23,516	6,271	....	....	....	....
Norway	18,839	46,818	25,313	50,654	....	50,620	....	....
All others	57,880	588,302	32,000	533,122	....	....	....	....
Total	1,122,131	1,251,069	1,285,398	1,314,061	....	....	....	....

Figures not shown not available. Figures taken from Tables 15. "All others" taken from International Institute of Agriculture, Rome, Italy.

5. World Production of Nitrogen.

Table 17 shows the world production of nitrogen in net tons of nitrogen for the years 1910 and 1920, inclusive, listed according to the kind of nitrogen, viz, nitrate nitrogen, by-product nitrogen, and atmospheric nitrogen. The figures for total fixed atmospheric nitrogen show very clearly the growth of this industry. However, it must be borne in mind that a large part of the increased war production is from plants not capable of economic commercial production.

TABLE 17.—*World production of nitrogen.*

(In net tons of nitrogen.)

	1910	1911	1912	1913	1914	1915
Chilean nitrate	[1] 423,943	[1] 433,505	[1] 444,653	[2] 455,906	[2] 413,127	[2] 294,534
By-product ammonia	[3] 221,510	[3] 240,667	[3] 268,130	[3] 305,099	[3] 271,823	[3] 309,304
Cyanamide process	[5] 4,058	[5] 10,792	[5] 20,778	[5] 35,838	[6] 44,035	[6] 168,336
Haber process	0	0	0	[6] 6,798	13,596	[6] 33,990
Arc and other processes	[4] 5,000	[4] 7,500	[4] 12,000	[5] 19,800	[6] 23,000	[4] 26,000
Total fixed atmospheric nitrogen	9,058	18,292	32,778	62,436	80,631	228,326
Total	654,511	692,464	745,561	823,441	765,581	832,164

	1916	1917	1918	1919	1920
Chilean nitrate	[2] 488,974	[2] 503,474	[2] 479,622	[2] 276,945	[2] 422,685
By-product ammonia	[3] 345,698	[3] 368,991	[4] 370,000	[4] 309,000	[4] 391,400
Cyanamide process	[6] 196,108	[6] 232,364	[6] 231,829	....	[4] 130,000
Haber process	[6] 67,980	[6] 113,300	[6] 192,610	....	[5] 297,000
Arc and other processes	[4] 29,000	[5] 33,000	[4] 40,000	....	[5] 42,130
Total fixed atmospheric nitrogen	293,088	378,604	464,439	....	469,130
Total	1,127,760	1,251,069	1,314,061	....	1,283,215

[1] Report of Federal Trade Commission on the Fertilizer Industry.
[2] American Fertilizer Handbook.
[3] From Table 13.
[4] Estimated from miscellaneous data.
[5] Final Report of Nitrogen Products Committee.
[6] International Institute of Agriculture, Rome, Italy.

Figures not shown not available.

CHAPTER III.

DEVELOPMENT OF NITROGEN FIXATION IN THE UNITED STATES AND FOREIGN COUNTRIES.

A. EARLY DEVELOPMENT.

The development of nitrogen fixation into one of the industries of the world had its inception about 20 years ago. As early as 1781 laboratory experiments had proven the possibility of fixing atmospheric nitrogen, but it was not until about 1900 that serious efforts were made to secure commercial production.

The assertion of Sir William Crookes in 1898 that the supply of Chilean nitrate would soon be exhausted and that the world would then starve unless some permanent source of nitrogenous fertilizer could be found had a marked effect in arousing the world to the coming importance of nitrogen fixation. However, the growth of the fixation industry has not been due in any way to actual exhaustion of the Chilean deposits, for they still contain enough raw material to last for a long term of years.

From 1900 to 1914 the consumption of nitrogenous materials in agriculture and industry increased steadily and rapidly, thus making a condition favorable to the substantial growth of the young industry while the World War with its pressing military demands gave it additional impetus.

A great number of processes have been suggested and tried out more or less thoroughly, but only three—arc, cyanamide, and direct synthetic or Haber—have obtained any considerable success.

1. Arc Process.

The arc process, the oldest of the three, has been able to survive only where hydroelectric power is very cheap, and the largest plants of this type are found only in Norway and Sweden.

The arc process went through a long period of early development before the first commercial plant was built.

Cavendish had noted the formation of nitric acid when hydrogen was burned in air in 1781, and in 1783 he found that an acid was formed when electric sparks were passed through air. In 1798 L. Odier explained the formation of nitric acid in the air as a combustion reaction, and in 1800 Sir Humphry Davy made nitric oxide by passing air over a platinum wire heated by an electric current. Later developments in the laboratory showed that lengthy discharges gave better results than short ones and that the air should be kept in motion. In 1870 Berthelot showed that the arc could displace the electric spark with improved results, and at the same time he showed that the reaction between the oxygen and nitrogen of the air is reversible; i. e., that the concentration of the oxides of nitrogen soon reaches a limit if the air is retained in the arc, beyond which dissociation of the oxides takes place as rapidly as their formation. The principles underlying the action of the magnetic field on the arc were first discussed by Arago in 1820, and were made the subject of experiment by Davy in 1821 and many later observers, including Pflücker, who made a detailed study in 1861.

These are essential facts, an understanding of which was fundamental in the design of a furnace which could produce nitric acid on a commercial basis, and, now that the principles of the reaction had been established, progress became dependent quite largely upon the development of electrical machinery and the solution of the various difficulties in the construction of a satisfactory furnace in which to bring about the reaction.

The apparatus used in the first attempt at industrial utilization consisted of an inclosed space with an arrangement of platinum wires so placed as to allow the passage of electric sparks between their ends. This unsuccessful attempt was made in 1859. The use of silent discharge along with the electric spark was tried without success in Germany. Other patents in 1895 and 1896 contained the essential principles for success, but no industrial installation was attempted.

The work of Bradley and Lovejoy has a very important place in the development of the arc process. Although their method did not meet with commercial success, it did lead directly to another method which has proved successful. The Bradley and Lovejoy method was patented in 1901, and a large plant was built at Niagara Falls in 1902. After a thorough test the works were closed down in 1904 after the yield had proved insufficient to render the enterprise commercially successful. Failure seems to have been due in large measure to the fact that the equipment was very costly and rather fragile, requiring frequent repairs. The corporation organized to undertake this work was called the Atmospheric Products Co. and was capitalized at $1,000,000.

The basic principle of the method was sound. It aimed at the formation of an enormous number of small slender arcs of short duration in order to bring a large quantity of air in contact with the arcs using a minimum of power. Each unit of apparatus consisted of an iron cylinder 5 feet long and 4 feet in diameter revolving upon its axis. A series of radial arms projected inward from this cylinder and terminated in platinum points. A corresponding series of arms with platinum points projected outward from the stationary axis. The cylinder formed one electrode and the axis the other. When the current was on and the cylinder was rotated, the platinum points passed at a short distance and an arc was formed which was drawn out in length, as the distance between the points increased, until the distance became too great and the arc was broken. Thus the air passing through the cylinder was constantly subjected to a great number of slender arcs of very short duration. A direct current at 10,000 volts was used.

While this work was in progress in the United States, the first really successful furnace was being developed in Norway by Christian Birkeland and Samuel Eyde. The method which they devised, when used with very cheap power, resulted in the first industrially successful plant for nitrogen fixation. In 1903 they built a plant to use 150 horsepower at Ankerlokken, near Christiania. In 1904 a plant to use 1,000 horsepower was put in operation near Arendal, and the next year the works at Notodden were put in operation with 2,500 horsepower. In 1907 they were using 40,000 horsepower, and in 1911 55,000 horsepower. In 1919 Notodden was using 60,000 horsepower, and works had been built at Rjukan using 290,000 horsepower, making the combined requirements of the two plants about 350,000 horsepower, both Schönherr and Birkeland-Eyde furnaces then being in use. The combined capacity of these two factories had reached about 30,000 metric tons of nitrogen per year.

The Schönherr furnace had been in process of development in Germany while Birkeland and Eyde were doing their important work in Norway. The excellent characteristics of the Schönherr furnace made it the chief competitor of the Birkeland-Eyde furnace in the great Norwegian works. A description of the three leading types of furnace—the Birkeland-Eyde, the Schönherr, and Pauling—will be found in Chapter IV under the arc process.

2. The Cyanamide Process.

The cyanamide process, which dates back to the patents of Frank and Caro, 1895–1898, is the most generally used process of the three and is not dependent upon any unusual set of conditions for its successful operation.

The discovery in 1901 that calcium cyanamide could be used directly as a nitrogenous fertilizer opened a great field for the new compound, and no effort was spared in pushing the technical improvement of the process. The problem consisted of the following factors—to get a cheaper method of extracting nitrogen from the air, to produce carbide more economically, to increase the percentage of nitrogen in the product, and to adapt the product to use as fertilizer.

Attempts were made to bring about the direct formation of cyanamide by heating lime and coke in an atmosphere of nitrogen, according to reaction

$$CaO+2C+2N=CaCN_2+CO.$$

This method was partly successful, but yielded a product low in nitrogen, and so was abandoned for methods using carbide as an intermediate product.

The use of salts, mixed with the carbide as catalyzers, to improve the absorption of nitrogen by the carbide was introduced at the very beginning of the industry. Calcium chloride was proposed in 1901 and fluorspar (CaF_2) in 1906. The calcium chloride assisted in the absorption of nitrogen, but the product containing calcium chloride gave trouble unless unusual care was taken to prevent exposure to moisture. The use of fluorspar gave better results, and its use, though by no means universally adopted, is still the practice at most plants. A method has been suggested by which the salt is added to the fused carbide as it leaves the furnace and the solid material exposed to an atmosphere of nitrogen when it reaches the proper temperature. But this material is too compact to allow satisfactory penetration of the gas, and the temperature of the fused material is too high to allow the completion of the cyanamide reaction. These facts have brought about the universal practice of cooling and pulverizing the carbide before treating it with nitrogen.

An abundant supply of nitrogen of low cost and high purity is essential. Moisture, oxygen, carbon monoxide, and carbon dioxide are impurities that can be tolerated only in very small amounts. Several chemical methods for producing pure nitrogen have been used, all of which are quite similar in principle of action to the copper-cupric oxide method. In this method air is passed through tubes containing heated copper shavings which remove the oxygen with the formation of cupric oxide. The oxide is reduced to the metal again by heating it in a current of some reducing gas. Two tubes are required to give a continuous supply of nitrogen. By mixing air and producer gas and passing it through a heated tube containing a mixture of copper and cupric oxide, followed by a purification system for removing carbon dioxide, a continuous supply of nitrogen can be obtained.

However, experience has shown that the mechanical methods based on the fractionation of liquid air are capable of supplying fairly pure nitrogen more economically than any of the chemical methods, and most of the nitrogen used in the cyanamide process at the present time is made by the use of Linde or Claude liquid air machines. In large installations of this type the cost of nitrogen has become a very minor item in the cost of producing cyanamide, so no material improvement along this line can be expected.

In adapting the crude cyanamide to use as fertilizer the industry has not been entirely successful. In most parts of the world the users of fertilizer still prefer other forms of nitrogen, such as ammonium sulphate or Chilean nitrate, even at higher unit cost. This probably, more than anything else, has limited the expansion of the industry, and has led to the conversion of a part of the production of cyanamide into more popular materials.

3. Direct Synthetic Ammonia Process.

The direct synthetic ammonia process is the newest of the three, and can be said to have had its beginning when, in 1905 and 1906, Prof. F. Haber, of Karlsruhe, with the aid of G. von Oardt, published a series of papers in which the general conditions for a successful solution were clearly defined. The process was first used in successful factory operation in 1913, but expansion took place very rapidly under war conditions, so that the process was used for nearly one-half of the nitrogen fixation capacity of the world in 1919. It had not been used successfully outside of Germany until 1921, when the development of the synthetic processes in England, France, Italy, and the United States showed genuine progress.

The Badische Anilin und Soda Fabrik control the process in Germany. The fundamental principles for successful plant construction had been worked out carefully before the war, so the company was ready for rapid expansion when the war made it necessary. Their first plant, at Oppau, which had a capacity of only 7,000 metric tons of nitrogen in 1913, was rapidly enlarged during the early part of the war, until its capacity reached 100,000 metric tons of nitrogen per year. The reaction chamber or bomb was enlarged from a tube about 3 inches in diameter to a cylinder about 3 feet in diameter and 40 feet long.

The various modifications of the synthetic process which are being developed outside of Germany have certain distinguishing characteristics. The direct synthetic plants in Germany use 200 atmospheres pressure, the American plant 100 atmospheres, and the Claude process in France 600 to 1,000 atmospheres. The Italian and French plants use electrolytic hydrogen; the German and American use producer gas or water gas as a source of hydrogen.

4. Résumé for 1913.

It was well understood long ago that the outcome of a great war might depend upon the ability of the combatants to obtain nitrogen compounds for their munitions supply. Germany fostered her nitrogen fixation industry for years before the war and as a result was able to continue the war after being cut off from the outside world. In other parts of the world the industry received no Government aid until after the outbreak of the World War.

At the end of the pre-war period the world's capacity for nitrogen fixation had reached about 85,000 metric tons of nitrogen per year; 7,000 tons by the direct synthetic process, 60,000 tons by the cyanamide process, and 18,000 tons by the arc and other processes. There were cyanamide plants in eight countries, arc plants in five countries, and one direct synthetic plant. Statistics on the location and capacity of the plants are conflicting, due probably to the existence of several small semiexperimental installations. This 85,000 tons of nitrogen, the fixation capacity in 1913, represented only 10 per cent of the world's requirements of fixed inorganic nitrogen, the other 90 per cent coming from Chilean nitrate and by-product ammonia.

Detailed estimate of the world's installations at the end of 1913 is as given in Table I.

TABLE I.

Country.	Number of plants.	Process.	Estimated capacity metric tons nitrogen.
Germany	1	Haber	7,000
United States	None.		None.
Total	1		7,0 0
Germany	3	Cyanamide	10,000
Austria	2	do	4,500
France	1	do	1,500
Norway and Sweden	2	do	17,000
Italy	3	do	7,000
Switzerland	2	do	5,600
Canada	1	do	11,400
Japan	1	do	3,000
United States	None.	do	None.
Total	15		60,000
France	2	Arc and miscellaneous	700
Norway	2	do	14,500
Italy	1	do	700
Spain	1	do	1,600
United States	1	do	500
Total	7		18,000

B. HISTORY OF NITROGEN FIXATION DURING THE WAR PERIOD.

As the war progressed, the important part that nitrogen fixation was to play became evident, and the countries of the world fell into three classes according to their dependence upon atmospheric nitrogen. In the first class we find those who were cut off from access to Chilean nitrate and who therefore were compelled to produce their own supply of nitrate for explosives if they were to continue the war. Germany and Austria belonged in this class. In the second class we find those countries which took part in the war and were able to secure Chilean nitrate, but, because of uncertainty as to their ability to secure a sufficient and continuous supply of Chilean nitrate, extended Government aid of some sort to the fixation industry as a means for national security. France, Great Britain, Japan, and the United States belong in this class. In the third class we find Norway, Sweden, Italy, Switzerland, and Canada, in which countries the industry was allowed to continue on purely commercial lines, the war having an effect only in making the business more profitable.

1. Germany.

Germany's position with regard to a nitrogen supply was most critical during the war. Her commerce with Chile was cut off early in the war, and it became imperative to produce, within her own borders, all the nitrogenous materials required for munitions as well as other essential uses. A Government nitrogen administrator was appointed and given authority to regulate the production and use of all nitrogenous materials. Under this control all sources of by-product ammonia were used to the fullest extent, without relieving the situation to any great extent. The Government built two large cyanamide plants from public funds and brought about the enlargement of existing cyanamide works and the construction of new ones by liberal loans. However, the main source of new supplies of nitrogen was developed at Oppau, where the Badische Anilin und Soda Fabrik had a plant using the direct synthetic process and producing about 7,000 metric tons fixed nitrogen in 1913. This plant was enlarged to a capacity of 100,000 metric tons nitrogen per year during the early part of the war, and another plant, located at Merserberg, was built with capacity for 200,000 metric tons nitrogen per year. About three-quarters of its capacity had been put in operation before the armistice. With the completion of the Merseberg plant Germany's total nitrogen capacity amounted to 570,000 metric tons per year; 300,000 tons by the direct synthetic process, 120,000 tons by the cyanamide process, and 150,000 tons from coal distillation. Along with the fixation works, Germany had built plants for the conversion of ammonia into nitric acid of all concentrations as required in her munitions factories.

Germany was limited by lack of power in choosing the process for her main war production. The tremendous power requirements of the arc process made it out of the question. Even the smaller power requirements for the cyanamide process made it impossible to get adequate nitrogen production by that process; but she was able to secure the trained personnel and high-grade equipment required for the direct synthetic process, and so naturally chose that process, possibly without considering comparative costs.

2. United States and Canada.

In Canada the plant of the American Cyanamid Co., at Niagara Falls, was enlarged just before the war from a capacity of about 32,000 tons of cyanamide to about 60,000 tons, or 12,000 metric tons of nitrogen, having been enlarged from 16,000 to 32,000 in 1911. Nearly the whole output of this plant has always been shipped into the United States. The plant of the American Cyanamid Co. was built in 1908, but did not get into regular production until some two years later. The first ammonia produced in North America from cyanamide was made late in 1915 in autoclaves built by the American Cyanamid Co. at one of the plants of the E. I. du Pont de Nemours Powder Co. The American Cyanamid Co. erected autoclaves also at the Ammo-Phos Works, at Warners, N. J. These were put into operation in January, 1917, and practically the whole output of ammonia throughout the war was marketed as aqua ammonia for use in explosives manufacture. The plant was built for the production of "Ammo-Phos," a new material for use as fertilizer, but the production of this material did not begin until after the armistice, owing to the demand for ammonia as such.

The United States Government built one synthetic plant with a nominal capacity of 8,000 metric tons nitrogen per year; also a cyanamide plant with capacity of 40,000 metric tons of nitrogen per year; and at the time of the armistice had two additional cyanamide plants under construction with a combined capacity of 40,000 metric tons. The detailed history of the activities of the Government in nitrogen fixation will be found in Chapter VII.

A small arc plant was built near Seattle, Wash., by the American Nitrogen Products Co., sodium nitrite being the main product of the company during the war.

3. Great Britain.

Great Britain was without fixation plants during the war. Her dependence on imports was a source of constant anxiety and resulted in laying the foundation for a direct synthetic plant. A committee, called the Nitrogen Products Committee of the Munitions Inventions Department, and composed of leading scientists and business men, was appointed to study the problem and advise the Government. This committee made a very thorough investigation, and in its final report made this recommendation:

> "As a minimum provision for safeguarding the future and for meeting a portion of the growing home demand for various nitrogen products the establishment in Great Britain without delay, either by private enterprise (supported, if necessary, by the Government) or as a public work, of a cyanamide plant with a nitrogen capacity of 12,000 tons per year."

During the first 10 months of 1918 Great Britain imported 583,000 short tons of Chilean nitrate, an amount four times as great as for a similar period before the war. In order to conserve the supply of nitrate the nitrate used in agriculture was almost entirely replaced by sulphate of ammonia.

4. France.

The French war program called for the construction of enough cyanamide plants to furnish nitrates in sufficient amount to replace Chilean nitrate in all her munitions factories. This program had not been completed at the time of the armistice, but a considerable part of the work had been done toward increasing the country's pre-war capacity of about 2,000 metric tons of fixed nitrogen up to 60,000 metric tons per year. Six large ammonia oxidation plants were built, or were under construction at the time of the armistice, for converting part of the ammonia produced at the cyanamide plants into nitric acid. All of the oxidation plants were owned by the Government, as were two of the cyanamide plants, and the other seven cyanamide plants received liberal Government assistance. Although these plants were producing considerable fixed nitrogen at the time of the armistice, Chilean nitrate was still being imported at about the pre-war rate, and consumption was just about equal to combined production and imports. During the war feeling in France was very strongly in favor of continuing the nitrate program after the war by placing a tariff upon imports of nitrate of soda sufficient to cover the difference in cost between it and synthetic nitrates from the French factories. During the first 10 months of 1918, the imports of Chilean nitrate into France amounted to 340,000 short tons.

5. Japan.

In Japan the cyanamide capacity was doubled and steps were taken toward the installation of a synthetic plant. Japan had been the leading importers of ammonium sulphate before the war, and when this source of supply was cut off by the demand for the sulphate in the producing countries it left the domestic producers in an unusually favorable position, especially since sulphate is a very popular form of nitrogenous fertilizer in Japan.

6. Italy.

In Italy the industry received no Government assistance in financing expansion. However, the business was profitable during the war and grew from a capacity of 7,000 metric tons of nitrogen per year before the war to about 20,000 metric tons of nitrogen after the war. Nearly all of the capacity built during the war used the cyanamide process. During the first 10 months of 1918 Italy imported 94,526 short tons of Chilean nitrate, which is considerably in excess of pre-war consumption.

7. Norway, Sweden, and Switzerland.

The nitrogen fixation business was especially prosperous in Norway during the war. At the great arc process plants there was still opportunity for enlargement of the power plants. This was done and the capacity of the arc plants doubled. The cyanamide capacity of all these countries was increased, the total increase in capacity amounting to about 6,000 metric tons of nitrogen per year.

C. HISTORY SINCE THE WAR AND PRESENT STATUS.

Since the war the disturbed condition of the world's commerce and finance has made progress in all lines of industry erratic and uncertain. However, the nitrogen fixation industry has stood the trying times very well and is progressing along certain lines as indicated below:

1. Development of direct-synthetic processes in the United States and England, and of the Claude process in France.
2. Development work on new processes, as, for example, the Mehner process, at the Skoda Works in Austria.
3. Efforts to use war plants for fertilizer production, especially in the United States and France.

1. Germany.

The nitrogen industry has probably fared better in Germany than in any other country since the war. A combination of all the interests producing nitrogen products has functioned successfully and has kept the various interests—direct synthetic, cyanamide, and by-product coke ovens—in harmonious cooperation. According to recent reports the 1920 production by the different processes was about as follows: Ninety thousand metric tons nitrogen by cyanamide process, 270,000 metric tons nitrogen by direct synthetic process, and 100,000 metric tons from the by-product coke ovens. In comparing this with the capacity as given in Table IV, i. e., cyanamide 120,000, direct synthetic 300,000, and by-products from coal 150,000, it must be remembered that a considerable part of the cyanamide capacity was built merely for war purposes and for various reasons can not meet commercial conditions. The poor showing of the by-product coke oven is due to the depressed condition of the iron and steel industry which determines the output of the coke ovens. It is interesting to note that the output of the direct synthetic plants as reported is 90 per cent of the maximum capacity as given in Table IV. It is reported that aqua ammonia has been exported to Scandinavia by tank cars and car ferry for use in making ammonium nitrate at the great arc plants.

2. United States.

In the United States the development of the direct synthetic process has been pushed forward energetically since the armistice by the General Chemical Co., and since the organization of the Allied Chemical Co., by the Atmospheric Nitrogen Corporation, which was organized for the purpose of completing the development of the process as started by the General Chemical Co.

As soon as it was decided that the General Chemical Co. should not take over the work at United States Nitrate Plant No. 1, the company began the design of a plant in which the errors made at United States Nitrate Plant No. 1 should be corrected. This work was taken over by the Atmospheric Nitrogen Corporation, and the first unit of the plant has been built at Syracuse, N. Y. This first unit of 10 tons of ammonia per day capacity was put into operation in August, 1921, and is reported to be giving excellent results. Although the plant is not large, so far as nitrogen capacity goes, yet it is of great importance as a key plant from which to expand should the process prove to be profitable. Since the product is obtained in the form of liquid ammonia, the process has the advantage of the differential in price between liquid ammonia, which is used directly for refrigeration, and other forms of ammonia. This advantage is, of course, limited to the demand for ammonia in the anhydrous state. This plant is located at the works of the Solvay Process Co., at Syracuse, N. Y., and therefore will be able to benefit from any advantage that may come from operating the process in connection with the ammonia-soda process. The Atmospheric Nitrogen Corporation is strongly connected with large, well-established manufacturers of chemicals.

The history of the synthetic ammonia plant, called United States Nitrate Plant No. 1, will be found in Chapter VII of this report. As this plant failed to function and as there is little prospect that any governmental attempt will be made to make it capable of production, it need not be counted in figuring the nitrogen fixation capacity of the country.

The big cyanamide plant, called United States Nitrate Plant No. 2, is being maintained in stand-by condition by the War Department. This plant has a capacity of about 40,000 metric tons of nitrogen per year and is fully described in Chapters IV and VII.

The American Nitrogen Products Co., of Seattle, Wash., owns a small arc plant producing as its product sodium nitrite. The capacity of this plant is about 300 metric tons of nitrogen per year.

3. Great Britain.

There is only one nitrogen fixation plant of commercial importance in Great Britain. This is the Synthetic Ammonia & Nitrates (Ltd.), a company formed by Brunner-Mond & Co. (Ltd.), with a capital of £5,000,000, to take over from the Government the plant which had been started by the ministry of munitions at Billingham, Durham. During the war there were some experimental plants, but these, it is understood, have now been abandoned.

The Synthetic Ammonia & Nitrates (Ltd.) was formed in June, 1920, and their plant thus far is not yet completed. At the time the project was taken over from the Government a certain amount of preparatory work in connection with the building of the factory had been accomplished. This work, suspended at the armistice, is now being completed by the company whose plans provide for a plant with capacity of 100 tons of 100 per cent ammonia per day, with provision for expansion to 300 tons per day. This company occupies a very favorable position in the chemical field because of its connection with Brunner-Mond & Co., one of the oldest organized chemical companies of Great Britain, and which has long been engaged in the manufacture of sulphate, carbonate of soda, and soda ash. The British Government has made an agreement with the company that it is always to be British controlled and has agreed to give the company every possible assistance for the purpose of developing the process, protecting the company against German interference in the development of the process in England. Much can be expected from this enterprise entered into under such favorable circumstances.

4. France.

There has been very little material progress in the industry in France since the war. Attempts are still being made to use some of the war-created facilities in the establishment of a peace-time industry, but present reports are to the effect that none of the fixation plants in France are in operation.

The promoters of the Claude process have been very active in perfecting the process and in advertising its advantages, but it will take time to tell whether it is superior to the Haber process for large installations. There is a movement on foot to enlarge the present Toulouse plant with a view to making it the principal plant for nitrogen fixation in France, and a study has been made by a commission to determine whether or not the Haber or the Claude process will be employed. As far as known, no final decision has been reached.

The only arc plant recently operated in France has been closed down, due to the expiration of the favorable power contract which made its operation possible. It is quite improbable that this plant will again operate.

5. Japan.

In Japan rather extensive plans for enlargement of the industry were made after the armistice. Among these was a project for the establishment of a direct synthetic plant in Japan. However, the financial panic which came as a result of the war inflation has made necessary the indefinite postponement of these enlargements. It is therefore believed that the nitrogen industry in Japan is very much as it was at the time of the armistice.

In certain reports the capacity of Japan for the production of nitrogen compounds both by fixation and by the by-product coking of coal seems to have been greatly exaggerated. In his testimony before the Senate Committee on Agriculture and Forestry Doctor White gives the maximum capacity of Japan for the production of fixed atmospheric nitrogen as 20,000 metric tons per year. The American Fertilizer Handbook for 1919 gives Japan's production of sulphate of ammonia as about 2,000 tons per year. S. Kuroda gives the by-product ammonium sulphate production of Japan for 1917 as 14,000 tons. He gives the cyanamide production in 1917 as 50,000 tons and says that the cyanamide is the only nitrogen fixation process used in Japan. Reports have been noted giving the Japanese production of ammonium sulphate as high as 100,000 tons per year, but this is believed to be much too high and probably refers to the amount consumed and so includes imports as well as domestic production. Taking the iron and steel production as a basis for an estimate, it seems quite improbable that the by-product ammonium sulphate production could exceed 25,000 tons per year, assuming that all the coke is made in by-product ovens. A part of the cyanamide production is converted into ammonium sulphate, one company having been reported to have made 16,000 metric tons by this method in 1919.

6. Italy.

Italy has a prosperous and well-established fixation industry consisting of four active cyanamide plants, two arc plants, and one small synthetic ammonia plant. There is a good market for the products in Italy, and production has been maintained at a very fair proportion of the capacity of the plants even since the war, when the country has been in a distracted condition industrially. Present reports to the effect that the industry is seriously depressed are believed to refer to a temporary condition.

The Italian Government has afforded no support to these industries, either directly in the shape of subsidies or loans, or indirectly through mitigation of the burdens of taxation or the imposition of a protective tariff.

The following plants have been established in Italy for the manufacture of nitrogen products:

1. Società Italiana Carburo di Calcio, Terni, Umbria.
2. Società Agroria di Domodessela, Domodessela.
3. Societá Piemontese Carburo di Calcio, S. Mucel, Vald, Aosta.
4. Società Italiana Industriale, Asceli Piceno, Nocerata.
5. Dott, Rossi, Officine Elettrochimiche, Legnano.
   Dott, Rossi, Officine Elettrochimiche, Ponto Mammelo, Rome.
6. Società Idros, Terni, Umbria.

Of these plants the first four use the cyanamide process and are owned by the Società Italiana per la Fabbricazione di Prodotti Azotati, with its main business office at 66, via Due Mocelli, Rome.

The yearly capacity of these cyanamide plants, when running full capacity, is stated to be as follows:

The plant at—	Metric tons.
Terni	45,000
Domodessela	15,000
S. Marcel	5,000
Arceli Piceno	8,000

The two plants listed under No. 5 in the above list are arc plants. They are equipped for making nitric acid, sodium nitrate, and potassium nitrate. They are both of rather small capacity, details of which are lacking.

The plant listed under No. 6 is a modification of the Haber process. It has a capacity of only a few hundred pounds of anhydrous ammonia per day, but is said to operate economically and profitably in the production of liquid ammonia for refrigeration, and enlargements are in progress. One of the novel features of this plant is the use of electrolytic hydrogen.

7. Norway and Sweden.

The activities in nitrogen fixation in Scandinavia since the war have been mainly along the line of readjustment to new market conditions. The war demands of the Allies had made the business very profitable during the war, and since the war systematic efforts are being made to use the installed capacity for peace-time products. It is reported that during the early part of 1921 none of the cyanamide plants were in operation. Ammonium nitrate is one of the staple products of the arc plants which have been in operation, but it is reported that ammonia has been purchased from Germany for this purpose in preference to producing it at the domestic cyanamide plants. The estimated cost of power is about $4 per kilowatt year. The very low cost of power has given the arc process a foothold here such as it has found in no other part of the world. It is reported that production has gained on consumption during 1921, so that stocks of nitrate of lime and nitrate of ammonia have become rather large. This is due to falling off of demand due to general economic depression in the consuming countries.

8. Canada.

The only cyanamide plant in Canada is that of the American Cyanamid Co. at Niagara Falls. This plant has been in operation for over 10 years and has a capacity for about 12,000 metric tons of nitrogen per year. Almost the whole output of the plant is marketed in the United States, a part of it being converted into ammonium phosphate at the Ammo-Phos Works of the American Cyanamid Co. on Staten Island Sound, N. J.

The American Nitrogen Products Co., in addition to its plant in Washington State, owns a small arc process plant in British Columbia. It is understood that the company uses off-peak hydroelectric power.

9. Holland.

The fixation of nitrogen is only in its infancy in Holland. The first plant was built in 1918 as a result of the shortage of nitrogenous materials brought about by the war. It was built by private enterprise, but received some assistance from the Government.

It is reported that the Bucher process is used; that the plant has a capacity for the fixation of 2,500 metric tons of nitrogen per year, and that ammonium sulphate is produced. During the early history of the plant's operation the Government purchased the product, but since 1919 the company has been selling in the commercial market.

Although this plant was built as a result of acute war conditions, yet it was the intention that it should be continued after the war. Steam power is used, Holland having no water power. Information is lacking concerning the more recent activities of this plant.

10. Austria.

The main items of interest in nitrogen fixation in Austria since the war is the work which has been done on the Mehner process at the Skoda works. This process is a form of cyanide process and is novel in that it depends upon the circulation of molten iron for the maintenance of the temperature. No noteworthy changes in the producing capacity of the industry have been reported.

11. Switzerland.

In Switzerland the activities of the industry since the war have been mainly along the line of readjustment to peace conditions with greatly reduced production. Some of the manufacturers discontinued production entirely at the end of the war while most of them continued operation on a reduced scale.

12. Résumé for 1921.

While some of the best authorities estimate that the present nitrogen fixation capacity of the world is no greater than it would have been had there been no war, yet it is a fact that development has in some cases been quite different from what might have been expected had peace continued. Plants which have been built for the war emergency only may not be able to meet peace-time competition and should not be included in the substantial development since 1913.

Details of the present installations and present capacity, together with estimated commercial capacity, are given in Table II. By commercial capacity is understood such capacity for production as can be used in peace time for supplying the ordinary demand for nitrogen, and is used to differentiate from capacity usable only in time of war. The figures for commercial capacity were obtained by making deductions for plants believed to be unable to meet peace-time competition because of unfavorable location, or power conditions, or for other reasons. These figures are at the best only approximate, but they show the trend of the industry, and are given for that purpose. It is too early to say which of the war-created plants will be continued as a part of the world's peace-time industry. This can be determined only by the slow but sure application of the law of the survival of the fittest.

TABLE II.

Country.	Number of plants.	Process.	Estimated maximum capacity, metric tons nitrogen.	Estimated commercial capacity, metric tons nitrogen.
Germany	2	Direct-synthetic	300,000	300,000
United States	2	do	11,600	3,600
Total	4		311,600	303,600
Germany	7	Cyanamide	120,000	93,000
Austria	2	do	22,000	22,000
France	9	do	58,000	40,000
Norway and Sweden	3	do	28,000	28,000
Italy	5	do	18,000	12,000
Switzerland	3	do	7,000	7,000
Canada	1	do	12,000	12,000
Japan	4	do	20,000	12,000
United States	1	do	40,000	40,000
Total	35		325,000	266,000
France	2	Arc and miscellaneous	1,300	None.
Norway and Sweden	2	do	30,000	30,000
Italy	2	do	1,200	1,200
Canada	1	do	800	800
United States	1	do	300	300
Holland	1	do	2,500	2,500
Total	9		36,100	34,800

The estimated commercial capacity amounts to 604,400 metric tons of nitrogen per year. This corresponds with 85,000 tons in 1913, and is more than seven times as great as the 1913 capacity.

During the period 1913 to 1921, the arc process barely doubled, the cyanamide increased from 60,000 to 266,000 tons of nitrogen, and the direct-synthetic process increased from 7,000 to 303,600 tons of nitrogen per year. The capacity of all other processes is so small as to be almost negligible.

Statistics are not yet available on the actual production for the year 1920. However, it is quite certain that the 1920 production fell short of the estimated commercial capacity by a wide margin, due mainly to idle plants in the United States and France.

Table III gives the world's production of fixed inorganic nitrogen. Actual production is given for 1909, 1913, and 1917, but the figures for 1921 refer to maximum capacity for production and not to actual production. In this table no account is taken of organic nitrogen such as occurs in cottonseed meal, blood, tankage, etc. Although such organic materials are important in agriculture and in this field are interchangeable with the inorganic materials, they are by-products of other industries and so are limited in supply. Organic nitrogen is not available for use in the manufacture of munitions or for many other industrial purposes. The relation of these materials to the demand and supply of nitrogen has been covered in detail in Chapter II.

TABLE III.—*World's production of fixed inorganic nitrogen.*

[Expressed in metric tons of nitrogen.]

	1909	1913	1917	1921[1]
Chilean nitrate	300,000	390,000	392,000	500,000
By-product ammonia	212,000	343,000	364,000	423,000
Atmospheric nitrogen:				
Cyanamide process	2,500	60,000	200,000	325,000
Haber process	....	7,000	110,000	311,600
Arc and miscellaneous processes	3,000	18,000	30,000	36,100
Total	517,500	818,000	1,096,000	1,595,700

[1] Estimated maximum possible production.

From this table we find that only 1 per cent of the world's supply of inorganic nitrogen came from the air in 1909; it had increased to 10 per cent in 1913, and to 33 per cent in 1917; and that in 1921, 42 per cent of the total capacity for the production of inorganic nitrogen was atmospheric nitrogen fixation. Present indications are that the actual 1921 production will fall short of the figures given under 1921 which refer to total capacity. It seems quite likely that the production of Chilean nitrate and by-product ammonia will also fall short of maximum capacity in about the same ratio as production of atmospheric nitrogen, in which case 42 per cent of the actual production will be from the air.

Table IV shows the relative position of the countries of the world in domestic nitrogen resources, taking into account the population. The figures for nitrogen capacity are those for the maximum estimated capacity for 1921. The population figures were taken from an atlas in 1920 and have not been corrected for the 1919 census, since more recent figures on the population of foreign countries are not available. This table shows Germany and Scandinavia easily in the lead, with Great Britain, Canada, France, Switzerland, and the United States in about the same class, but with the United States at the foot of the class, and Austria and Italy in the lowest places on the list. Even with the large increase in nitrogen capacity brought about by the war, Germany and Scandinavia are still the only world powers really independent in their nitrogen supply.

TABLE IV.—*Domestic sources of inorganic fixed nitrogen (maximum) in 1921.*

[Expressed in metric tons of nitrogen.]

Countries.	Population from 1920 atlas.	By-products from coal.	Atmospheric nitrogen.			Total.	Tons nitrogen per million population.
			Arc.	Cyanamide.	Haber.		
Germany	65,000,000	150,000		120,000	300,000	570,000	8,760
Norway and Sweden	8,000,000		30,000	28,000		58,000	7,250
Great Britain	45,000,000	100,000				100,000	2,240
Canada	7,200,000	3,000	800	12,000		15,800	2,200
France	40,000,000	15,000	1,300	58,000		74,300	1,850
Switzerland	3,800,000			7,000		7,000	1,840
United States	103,500,000	115,000	300	40,000	11,600	166,900	1,610
Austria	51,000,000	10.000		22,000		32,000	630
Italy	35,000,000	3,000	1,200	18,000		22,200	630
Other countries		27,000	2,500	20,000		49,500	
Total		423,000	36,100	325,000	311,600	1,095,700	

CHAPTER IV.

NITROGEN FIXATION PROCESSES.

A. CYANAMIDE PROCESS.

1. Description of Process.

The cyanamide process for the fixation of atmospheric nitrogen is based on the fact that when gaseous nitrogen, N_2, is passed over calcium carbide, CaC_2 heated to an elevated temperature, it combines to form calcium cyanamide, $CaCN_2$, essentially as represented by the equation

$$CaC_2+N_2=CaCN_2+C.$$

Before entering on the more detailed description of the cyanamide process, its essential features will be very briefly outlined.

The raw materials for the process are limestone and some form of carbon, either charcoal, anthracite coal, or coke, the latter being generally used. The nitrogen is ordinarily obtained by the fractional distillation of liquid air.

There are three principal steps in the cyanamide process proper—the production of calcium carbide, which involves, first, the burning of limestone to lime, and then the fusing of the lime with coke in an electric furnace; the isolation of nitrogen from the air in a rather pure state; and, finally, the treatment of the finely powdered, highly heated carbide with nitrogen, resulting in the fixation of the nitrogen.

The crude product is a grayish black solid containing about 60 per cent calcium cyanamide (21 per cent nitrogen), 20 per cent free lime, 12 per cent free carbon, and small amounts of iron and aluminum oxides, silica, etc. This product is variously termed lime-nitrogen, nitrolim, calcium cyanamide, cyanamide, cyanamid, and, in Germany, Kalkstickstoff. In this report it will be referred to as cyanamide, or where necessary more specific terms, such as calcium cyanamide, crude cyanamide, etc., will be employed.

a. Raw materials.—The quality of the raw materials for carbide manufacture is of importance not only because the contained impurities will appear in the final product but also because certain impurities interfere with the smooth operation of the furnace and also increase the energy requirement.

The manufacture of carbide for lighting and welding purposes has now become practically standardized, and consequently certain limitations as to the quantity of impurities which may be present in the raw materials have been established. Similar specifications of materials for cyanamide-carbide, however, have not been formulated, but in general no distinction is drawn between them. It has been suggested[1] that raw materials of lower quality may be employed in the manufacture of carbide to be used for cyanamide than for lighting and welding purposes.

The principal impurities in limestone rock are compounds of magnesium, silicon, iron, and aluminum. There are frequently present, also, small quantities of phosphorus and sulphur compounds, and in some cases clayey material. Bingham[2] gives the following as the maximum quantity of impurities permissible in limestone for carbide manufacture: Magnesia, 0.50 per cent; iron and aluminum oxides, 0.50 per cent; silica, 1 to 1.2 per cent; phosphoric acid (P_2O_5), 0.01 per cent; and only traces of sulphur. Such a limestone would contain 97 to 98 per cent of calcium carbonate.

The impurities, ash constituents, contained in coke or anthracite coal are essentially the same as in limestone, although the iron and sulphur content is very frequently higher. A source of carbon with a low ash is, of course, desirable in keeping the percentage of total impurities as low as possible.

The influence of various impurities in the raw materials for carbide manufacture has been investigated by Bingham[3] and also by Witherspoon.[4] Magnesium and aluminum compounds decrease the fluidity of the carbide, thus interfering with the smooth working of the furnace and causing trouble in tapping. Moreover, a greater energy input is required for high magnesia limes. The use of a fluorspar flux has been suggested as a means of counteracting the effect of magnesia. It may be pointed out in this connection that the presence of the fluorspar in carbide might also be advantageous if the latter is to be nitrified, since the catalytic effect of fluorspar on the nitrification reaction is well established.

The presence of silicon tends to increase the fluidity of the carbide and in that respect is beneficial. However, in the presence of iron, ferrosilicon is formed, and under certain conditions gives serious furnace trouble and, moreover, difficulties are also encountered in grinding carbide containing it. Carbide high in silicon is unsuited for acetylene generation, but the silicon appears to have no detrimental influence on the formation of calcium cyanamide.

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[1] Final Report N. P. C. P. 114.
[2] The Manufacture of Carbide of Calcium. Raggett & Co., London, 1916. P. 92.
[3] Loc. cit., 2.
[4] J. Soc. Chem. Ind., 32, 113 (1913).

Phosphorus is perhaps the most objectionable element in carbide not only for acetylene generation, but also for the production of calcium cyanamide which is later to be converted into nitric acid by oxidation of ammonia obtained from it. Fortunately, the quantity of phosphorus present in most limestones is so low that very little trouble is experienced. The phosphorus, originally present as calcium phosphate, is reduced in the furnace to calcium phosphide and appears as such in the carbide and later in the cyanamide, where, on treatment with water, phosphine is formed. The presence of even exceedingly small quantities of phosphine in the ammonia-air mixture appears to materially reduce the oxidizing efficiency of a platinum gauze catalyst.

While large amounts of sulphur in carbide are objectionable, it appears to be much less injurious to platinum gauze catalysts than is phosphorus.

In connection with the preceding statements as to the quality of limestone required, the data obtained during the trial run of United States Nitrate Plant No. 2 are of interest. The quality of limestone used at this plant is shown in the following analysis, which is the average for 145 carloads of stone:

	Per cent.
Calcium carbonate	96.41
Magnesium carbonate	2.37
Silica	0.77
Iron and aluminum oxides	0.45

It will be noted that the magnesium carbonate content is very much higher than the limit of 1.07 per cent (0.50 per cent MgO) set by Bingham. No particular difficulties in carbide furnace operation were encountered and a comparatively high furnace efficiency was obtained, as will be discussed later.

b. Limestone burning.—The conversion of limestone into lime is a necessary preliminary step in the production of carbide since the direct use of limestone in the electric furnace has not in general proven to be economical. This conversion is effected by heating the partially crushed rock to a temperature of about 1,100° C. until practically all of the carbon dioxide has been evolved. The chemical change occurring in the burning of limestone (calcium carbonate) to lime and carbon dioxide is represented by the equation:

$$CaCO_3=CaO+CO_2.$$

The process may be carried out either in vertical or in rotary kilns, but the latter are preferred for burning lime which is to be used for carbide manufacture because of the uniformity of product obtained.[5] The limestone rock is charged into the upper end of the slightly inclined and slowly rotating kiln, while the fuel, which may be either powdered coal, oil, or gas, is introduced through a burner at the lower end. The rock is gradually decomposed in its very slow movement down the kiln and the liberated carbon dioxide is swept out with the furnace gases. The burnt lime issues from the discharge end of the kiln at about 1,100° C. and passes through coolers, which are similar in construction to the limekilns, but smaller and unlined, where its temperature drops to 200° to 150° C. The lime is then discharged into conveyors which transfer it to storage bins.

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[5] The Manufacture of Lime for Chemical and Metallurgical Purposes. Richard K. Meade. Chem. and Met. Eng., vol. 23, pp. 841, 873, 929. (1920.)

The choice of fuel for lime burning is very largely determined by economic considerations. There are cases, however, where the ash from coal would be objectionable, since some 40 per cent of it would appear in the lime. Although coal ash is not particularly objectionable in cyanamide-carbide, a coal with relatively high ash very frequently leads to the formation of rings of semivitrified material in limekilns which obstruct the passage of the material. Their removal necessitates a shut down, resulting not only in a lowering of the kiln efficiency but also in injury to the kiln lining due to the large and relatively rapid temperature changes.

Meade [5] has estimated the fuel requirement for burning limestone as being from 2,800 to 3,500 B. t. u. per pound of lime or 400 to 500 pounds of coal, 37 to 45 gallons of oil, or 5,000 to 6,000 cubic feet of natural gas per ton of lime. Approximately 40 per cent of the total heat supplied to the kilns is lost as sensible heat of the exhaust gases, of which about 75 per cent could be recovered by the use of waste-heat boilers. Of the remaining 60 per cent of the heat supplied, about 54 per cent is used in the decomposition of the limestone and 6 per cent is radiated from the kiln shell.

The fuel consumption in burning limestone at United States Nitrate Plant No. 2 was higher than given by Meade. At this plant the limestone was burned in coal-fired rotary kilns, 8 by 125 feet, having a rated capacity of 100 tons of lime per 24 hours. During a 14-day run approximately 3.3 pounds of lime were burned per pound of coal, corresponding to about 600 pounds of coal per ton of lime. The coal used was high in ash, causing occasional shut downs due to ring formation. This, together with the fact that the kilns were new, undoubtedly accounts for the higher fuel consumption.

c. Lime fines.—The formation of lime fines, or powder, is a very serious factor in burning lime for carbide production. For the latter purpose it is preferable to have lime in the form of lumps about 1 inch in diameter, although any material over one-fourth inch is generally used. The fines prevent the free escape of the very large quantities of carbon monoxide gas produced in carbide formation, which may result in serious explosions, and furthermore the dust is very objectionable to the furnace operators.

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[5] Loc. cit., p. 71.

That most of the fining takes place in the lime coolers is shown by tests carried at United States Nitrate Plant No. 2. The following figures, the result of screen analyses made during the test, illustrate this point:

	Raw stone.	After kiln.	After cooler.
	Per cent.	*Per cent.*	*Per cent.*
Through ½-inch screen	11.0	17.1	41.0
Through ¼-inch screen	2.4	9.3	26.6

Further fining takes place in the conveyors and elevators which move the lime to the carbide furnaces. It was estimated that the over-all loss of lime by fining during the operations at the United States Nitrate Plant No. 2 amounted to 25 to 30 per cent of the total, assuming that all material passing through one-fourth-inch screen was lost.

The utilization of such large quantities of lime fines as would be produced at United States Nitrate Plant No. 2, for example, when operating at capacity is a serious problem unless a large, local market for building or agricultural lime is available. If a sufficiently cheap binder, such as coal-tar pitch, were available the briquetting of the fines for use in the carbide furnaces would probably be the most satisfactory solution of the problem.

As to the form and quality of carbon for the manufacture of carbide, it may be said that a nondusting material high in fixed carbon and low in ash is desirable. Charcoal, anthracite coal, and coke have been used. The use of charcoal has been practically discontinued, due mainly to the fact that a sufficient quantity can not be obtained at as low a cost as coal or coke. It is interesting to note in this connection that it is proposed to use charcoal for the manufacture of carbide at the cyanamide plant near Marignac, France. In this case the charcoal is a by-product in the distillation of waste wood and can presumably be obtained at a low cost. The objections to charcoal are that it usually contains only about 56 per cent fixed carbon, that it is extremely light and brittle, resulting in large losses in the form of dust, and that, according to Bingham,[2] it entails a high electrode consumption. On the other hand, the output is higher than with coal or coke and a higher quality of carbide can be obtained.

Coke for the manufacture of carbide should preferably be about three-fourths inch in size, soft burned as distinguished from metallurgical coke, not over 5 to 6 per cent in ash, and not over 0.5 per cent moisture.

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[2] Loc. cit., p. 70.

The choice between anthracite coal and coke for carbide manufacture is largely determined by cost considerations. In this country coke is very largely used.

d. Formation of carbide.—Calcium carbide is formed by fusion of a charge of lime and carbon in an electric furnace, the reaction being essentially as expressed by the equation:

$$CaO+3C=CaC_2+CO-121{,}150 \text{ cals.}$$[6]

It will be noted from this equation that an exceedingly large quantity of energy is absorbed in the formation of calcium carbide. It is this fact which makes necessary a very cheap source of power for the economical fixation of nitrogen by the cyanamide process.

It is also seen from the equation that a very large quantity of carbon monoxide is formed in the process, amounting for pure materials, for example, to 30 per cent of the weight of the charge. Since the heating value of carbon monoxide is about 4,380 B.t.u. per pound the possibility of utilizing this energy as a means of decreasing the power costs as a whole is an attractive one. A calculation shows that the energy of combustion of carbon monoxide produced in the reaction is equivalent to about 30 per cent of the energy required for carbide formation.

The use of carbon monoxide from carbide furnaces has been suggested for burning limestone.[7] Only a small percentage of the total quantity of gas would be required for this purpose, however.

In general no attempt is made to utilize either the combustion value of the carbon monoxide coming from the furnaces or its sensible heat. The chief obstacle would be that changes in furnace construction would be necessary which would greatly complicate the operation. The problem is such an important one, however, that a satisfactory solution should be found.

For the formation of carbide in accordance with the preceding equation, 10 parts of lime are required to 6.4 parts of carbon. In practice, however, an excess of lime is used to reduce the operating temperature of the furnace by lowering the melting point, which has the incidental advantage of facilitating the tapping of the furnace. The proportions are usually about 10 parts of lime to 5.8 parts of coke which contains approximately 85 per cent of fixed carbon.

The carbide furnaces are usually rectangular-shaped pits, with the upper edge flush with the main, or charging, floor of the furnace room. The walls and bottom are generally made of refractory brick and have a steel shell incasing them. They are placed along the side of the furnace room so that the molten carbide can be tapped off through a hole in the side into chill cars on the floor below.

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[6] Calculated Heat of Reaction. M. De K. Thompson. Trans. Am. Electrochem. Soc., vol. 16, 202 (1909).

[7] Final Report of Nitrogen Products Committee, p. 252.

In large furnaces particularly the masonry walls are protected from the intense heat of the furnace and the action of molten carbide by a layer of the partially fused charge. The bottom of the furnace is usually covered with a deep bed of refractory material, such as electrode carbon and coke. The electrodes are suspended above the furnace in such a manner that their depth in the charge is automatically regulated by a solenoid which controls a motor-driven hoist.

After the furnace has been started the mixed charge of lime and coke is shoveled in by hand, gradually increasing the depth of the charge. At the very high temperature of the furnace the lime fuses and reacts with the carbon to produce molten carbide. The furnace is tapped at intervals of about three-quarters of an hour, the time depending on the operating conditions, by opening the tap hole with a poker or electric needle, thus allowing the molten carbide to run into iron chill cars. The furnace should not be drained completely.

The efficiency of the furnace is dependent to a large degree on the skill of the operators. The composition of the charge and the size of furnace are also important factors.

The quality of the carbide can be materially influenced by the temperature and by the length of time between tappings, as well as by the proportions of lime and coke. The carbide obtained during the test run at United States nitrate plant No. 2 contained on an average 81.6 per cent CaC_2. This was obtained from the limestone previously referred to and coke containing 84 per cent fixed carbon and about 5 per cent ash.

The trend in carbide-furnace construction is toward very large furnaces. At United States Nitrate Plant No. 2, for example, the furnace units are 8,300 kv.-a., arc-resistance type, having inside dimensions of 22 feet 4 inches by 13 feet by 6 feet deep and a rated capacity of 48 tons of carbide per 24 hours. It is understood that larger furnaces than these have been installed by the American Cyanamid Co. at their plant at Niagara Falls, Canada.

A comparison of the operating efficiencies of the furnaces at United States Nitrate Plant No. 2 with those of other carbide installations on which data are available indicates that these furnaces are somewhat in advance of those formerly used in carbide manufacture. It is very probable, however, that the maximum efficiency of the furnaces was not reached during the comparatively short test period. The power consumption per short ton of 81.6 per cent carbide was 2,962 kw.-hr., which corresponds to 3,630 kw.-hr. per ton of 100 per cent carbide.

e. *Grinding of carbide.*—It is necessary to grind carbide to a very fine powder, at least 85 per cent through 200-mesh screen, before it is nitrified. For this degree of fineness the grinding operation is usually carried out in three stages. At United States Nitrate Plant No. 2, for example, the carbide, after cooling in the chill cars for 36 to 48 hours, is dumped onto a breaking platform, whereby it breaks into lumps of suitable size to enter a 30 by 42 inch jaw crusher, where it is reduced to 2-inch lumps or less. It is then ground in a ball mill until all of it passes a 10-mesh screen and about 90 per cent passes a 20-mesh screen. The final grinding is carried out in a tube mill, 85 per cent or more of the product passing through a 200-mesh screen.

In case a catalyst is used for nitrification, it is usually added to the carbide entering the tube mill. In this way a very intimate mixture is obtained.

Since carbide in a fine state of division readily reacts with the moisture of the air to generate acetylene gas, which forms explosive mixtures with oxygen, it is necessary to carry out all grinding and conveying of the carbide after it leaves the crushers in an atmosphere of nitrogen. Before starting the mills and conveyors therefore the air is swept out by nitrogen until the oxygen and acetylene percentages do not exceed 2 per cent and 1 per cent respectively. Frequently analyses for these two gases are made during operation.

f. Production of pure nitrogen.—Practically pure nitrogen, about 99.8 per cent, is necessary for the nitrification of calcium carbide. Nitrogen can be most economically produced in that state of purity by the liquefaction of air and subsequent distillation. Due to the highly developed state of gas-liquefaction processes the cost of nitrogen production forms a relatively unimportant part of the total cost of nitrogen fixation.

The supply of nitrogen is practically unlimited since this gas constitutes about 75 per cent by weight of the atmosphere. It has been calculated, for example, that the air over a single square mile of the earth's surface contains about 20,000,000 tons of nitrogen, which is thirty times the present yearly nitrogen fixation capacity of the world, and about fifteen times the present yearly consumption of the world.

In addition to nitrogen, which constitutes 75.5 per cent by weight and 78 per cent by volume, the principal gases and their respective percentages by weight and by volume are: Oxygen, 23.2 and 21 per cent; argon, 1.3 and 0.94 per cent; carbon dioxide, 0.04 and 0.03 per cent; and variable amounts of water vapor, depending on the temperature. Helium and neon are also present in the atmosphere to the extent of 0.001 and 0.002 per cent by volume, respectively, but due to their low boiling points—268.7° and 243° C.—they are not condensed in the production of nitrogen. Oxygen, carbon dioxide, and water vapor must be practically eliminated from the nitrogen which is to be used for carbide nitrification. Argon, being an inert gas, has no deleterious effect.

The basis of the method of separating air into its constituents was first suggested by Parkinson[8] in 1892 and depends on the difference of boiling points of liquid oxygen and nitrogen, these values being —182.5° and —195.5° C., respectively, at a pressure of 1 atmosphere. The simple distillation of liquid air does not affect a satisfactory separation, however, and it was not until in 1902, when Linde employed the principle of rectification, that the process became of commercial importance.

In liquefying air, use is made of the principle that when a compressed gas such as oxygen or nitrogen, or a mixture such as air, is allowed to expand, one obtains a marked cooling due to the Joule-Thomson effect, plus the effect due to any external work which the expanding gas is made to perform. For example, when air at 100 atmospheres pressure and ordinary temperature is allowed to expand freely down to 1 atmosphere the drop in temperature is about 25° C. However, since the boiling point of liquid air is —193 C. at a pressure of 1 atmosphere, it is seen that spontaneous liquefaction of air by simple expansion is not practicable. In actual practice, therefore, use is made of a heat interchanger, a device in which the cold, expanded gases are made to pass out around the tube containing the ingoing, compressed air and thereby decreases the temperature of the latter. With properly constructed apparatus the cumulative cooling effects obtained in this manner result in liquefaction of the air.

Two general types of air-liquefying process have been developed, both based on the principles mentioned above, but differing in the method of expansion.

In the Linde process, the gas is compressed to 200 atmospheres and expended by simple outflow, thus making use only of the Joule-Thomson effect. In the Claude process, the liquefaction of air is effected by expanding the gas in an ordinary compressed air motor, thus obtaining a cooling effect due to external work as well as to Joule-Thomson effect. This process has the advantages over the Linde process in that pressures only up to about 30 atmospheres need be employed and only a short time is required to reach the liquefaction temperature. It is for these reasons that it is rapidly gaining in favor for large installations and is the one installed at United States Nitrate Plant No. 2.

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[8] Industrial Gases. D. Appleton & Co., New York. P. 11. (1916.)

The liquefaction and rectification apparatus installed at United States Nitrate Plant No. 2 is shown in Figure 2. The temperatures and pressures noted on the drawing correspond to an actual test run on this apparatus. Valves, gauges, and other pieces of apparatus are numbered in accordance with the following tabulation. A study of this tabulation will greatly assist in obtaining an understanding of the operation.

1. Control valve of air entering exchanger.
2. Gauge for the pressure of the compressed air supplied to the apparatus.
3. Valve for inverting the compressed-air circulation in the exchanger.
4. Valve for inverting the oxygen and nitrogen circulation in the exchanger.
5. Valve for inverting the compressed air at the exit from the exchanger.
6. Exchanger for cooling the incoming air.

6a. Drain valve for purge bottle of exchanger.

7. Exchanger for cooling the incoming air.

7a. Drain valve for purge bottle of exchanger.

8. Gauge for the pressure of the compressed air at the expansion engine inlet.
9. Control valve for the expansion engine.
10. Expansion engine for cooling air by external work.
11. Liquefier for liquefaction of air.

11a. Drain valve for the liquefier.

12. Valve for throttling the liquid-air supply to same pressure as engine exhaust.
13. Lowest compartment of rectifying column.

13a. Drain valve for lowest compartment of rectifying column.

13b. Water level for the liquid rich in oxygen.

13c. Gauge for the back pressure in the lowest compartment of rectifying column.

14. Vaporizer tubes for liquefaction of air.

14a. Drain valve for bottom of vaporizer.

14b. Drain valve for second compartment in rectifying column.

14c. Mercury level of the vaporizer.

14d. Oxygen pressure gauge.

15. Valve for controlling the upflow of the liquid rich in oxygen.
16. Valve for the outlet of the impure oxgen gas.

16a. Cock for sampling waste oxygen.

17. Coil submerged in cooling liquid for liquefaction of nitrogen.

17a. Cock for testing the purity of nitrogen leaving the vaporizer and going to the condensing coil.

18. Inlet to the rectifying column of the liquid rich in oxygen.
19. Valve to control the flow of liquid nitrogen to the top of the column.
20. Top of the rectifying column.

20a. Water level for the liquid poor in oxygen.

20b. Nitrogen pressure gauge.

20c. Cock for the nitrogen test.

CLAUDE PROCESS
FOR
PRODUCTION OF PURE NITROGEN GAS

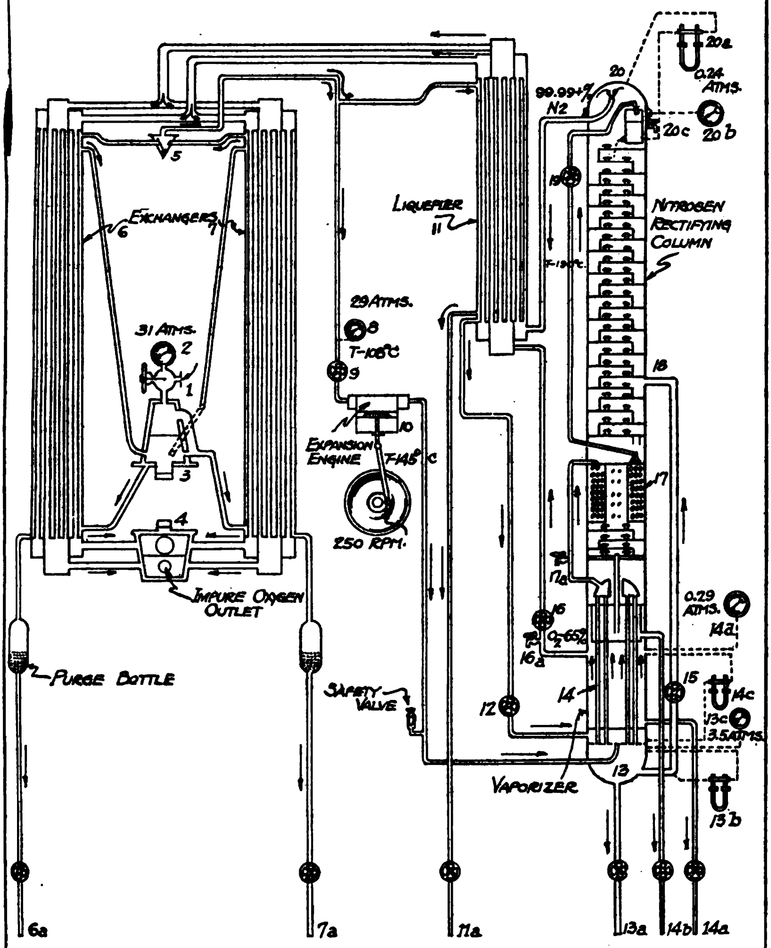

FIGURE 2

Use is made of air which has first passed through caustic soda towers to remove the carbon dioxide, and then through separators for the removal of caustic soda spray. This air is then compressed to 31 atmospheres, cooled in an aftercooler to the temperature of the cooling water available, and then enters through valve 1 into the space around the tubes of the first of the two heat interchangers, which are connected in series. It enters the first exchanger at the bottom of the jacket and passed upward to the top, and then enters the second exchanger at the bottom. Its temperature decreases progressively through interchange of heat with a downward flow of cold escaping gas, in the opposite direction to the flow of incoming air.

The cooling is accompanied by a partial condensation of the moisture in the air, the water dripping down and collecting in the purging bottle, while that part of the moisture which escapes condensation, together with any carbon dioxide left in the air, is deposited as snow on the surface of the tubes. Since the two exchangers are connected in series, most of the deposition of snow or solid carbon dioxide occurs in the second exchanger. When this deposition becomes serious the valves are thrown so as to reverse the order in which the two exchangers are connected, thus thawing out the one which was originally the cooler of the two.

The cold air from the top of the second exchanger passes to the expansion engine and liquefier, which are connected in parallel. About four-fifths of the air passes through the expansion engine and about one-fifth through the liquefiers. The temperature of the air entering the expansion engine is about —108° and its temperature drops to —145° because of the work which it performs in the engine. This expansion engine is a simple piston machine equipped with valves for air inlet and outlet. The air which enters the liquefier is cooled by gases from the rectifying column to a low enough temperature to liquefy.

The cold air from the expansion engine and the liquid from the liquefier both enter the lowest compartment at the bottom of the rectifying column. This compartment is provided with a baffle plate to reduce the pulsating effect of the exhaust from the expansion engine. A series of vertical tubes (14) called vaporizer tubes are connected into this baffle. The tubes are submerged in liquid dropped from the shelves of the rectifying column.

The pressure in the bottom compartment of the rectifying apparatus is about 3.5 atmospheres, while the pressure in the space surrounding the tubes of the vaporizer is only 0.29 atmosphere. This difference in pressure on the gas leads to a vaporization of the liquid surrounding the tubes and a partial liquefaction of the air in the tubes. The part of the air liquefied in the tubes drops to the bottom of the vaporizer and is richer in oxygen than the original air. This is the so-called principle of "backward return," patented by Claude.

The liquid rich in oxygen which collects at the bottom of the vaporizer is led through valve (15) and introduced into the rectifying column at point (18). The uncondensed gas, which is fairly pure nitrogen, is led through the condensing coil (17), which is submerged in a colder liquid than that which surrounds the pipes (14), sufficiently cold to liquefy nitrogen. The nearly pure liquid nitrogen from these coils is introduced through valve (19) into the top of the rectifying column at (20).

The vapor coming off from the top of the rectifying column is better than 99.99 per cent pure nitrogen. It has a temperature of about —190° and passes back through the liquefier, thus assisting in lowering the temperature of the original air which is liquefied. From the liquefier it then goes out through tubes of the heat exchangers.

The condensing coil (17) for the nearly pure nitrogen is immersed in a liquid which collects in the rectifying column at a point well toward the bottom of the column, where, however, the temperature of the liquid is low enough to condense the nitrogen. The liquid richest of all in oxygen which leaves the bottom of the rectifying column is that which surrounds the tubes (14) in the vaporizer and is evaporated as the original air condenses. This vapor also passes up through the liquefier and out through the heat exchangers in order to assist in the liquefaction and cooling of the original incoming air.

The total air entering an apparatus such as shown in this figure is 30,000 cubic feet per hour, of which, in normal operation, 24,000 cubic feet go through the expansion engine and 6,000 cubic feet through the liquefier. Two hundred horsepower are necessary for running the air compressors and about 6 horsepower for operating the circulating pumps for the carbon dioxide towers.

There are 30 units installed at Muscle Shoals, requiring a total of 6,180 horsepower, and they will produce per day of 24 hours 12,960,000 cubic feet of nitrogen, with a purity of 99.995 per cent, and 8,424,000 cubic feet of by-product oxygen of 50 per cent purity.

The boiling point of argon is —186.1° C., and consequently a part of it appears in the nitrogen, but the greater portion remains in the oxygen fraction. As previously mentioned, however, it is not objectionable in the nitrification process.

Among the by-products which may be obtained in the liquid-air process for nitrogen are oxygen, argon, helium, and neon, the first two being the more important. The oxygen obtained in this process is about 50 per cent pure, since up to the present time it has not been found possible to obtain simultaneously both nitrogen and oxygen in a high state of purity from the same equipment. It is stated that according to present practice the cost of producing pure oxygen from the 50 per cent gas is practically the same as from air. With the improvements which are still being made in liquefaction processes it appears probable that the simultaneous production of practically pure nitrogen and oxygen from the same apparatus may become possible.

There is, as a rule, a ready market for oxygen, the principal industrial uses at present being for oxy-hydrogen and oxy-acetylene cutting and welding. The extensive use of oxygen in a number of metallurgical operations appears to be dependent only on a cheap and abundant supply of this gas. It appears also that the by-product, oxygen from nitrogen fixation plants, can be utilized to excellent advantage in ammonia oxidation for enriching the air-ammonia mixture. The sale of by-product oxygen from nitrogen fixation plants is frequently limited or entirely prohibited by trade agreements, and consequently the oxygen is generally wasted. The profit from such sale, however, would be by no means a negligible factor in reducing the operating cost of the fixation process as a whole.

Practically all of the argon remains in the oxygen fraction and its separation from oxygen by chemical means is not very difficult. Argon is used to a large extent for filling electric lamp bulbs, and the demand for this purpose could, in a large measure, be met by the by-product argon from nitrogen fixation plants.

Helium and neon could be almost completely separated from oxygen and argon, and partially separated from nitrogen, by employing a second liquefier, from which a gas mixture consisting of about 50 per cent helium and neon and 50 per cent nitrogen could probably be obtained. The demand for neon is small, being limited very largely to the filling of tubes for use in wireless telegraphy and certain other electrical equipment.

Two other processes for the production of nitrogen which were used in the early days of the cyanamide industry, but which have now been completely displaced by the liquid-air process, may be mentioned at this point. The copper process consists essentially in passing air through an externally heated tube filled with copper turnings, whereby the oxygen combines with the copper, to form copper oxide, while the residual nitrogen passes through to the nitrifying ovens. The oxide is reduced to the metal again by heating it in a current of some reducing gas.

The Caro[9] process consists in passing producer gas through a heated mixture of copper oxide and copper which serves to burn the carbon monoxide and hydrogen to carbon dioxide and water. The gas mixture then contains only nitrogen and carbon dioxide, the latter being readily scrubbed out by alkali. This process has found only limited application.

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[9] Zeit. angew Chemie, p. 1178 (1909).

g. Nitrification of carbide.—The actual fixation of nitrogen by the cyanamide process is accomplished by bringing the practically pure nitrogen gas under slight pressure into contact with finely ground carbide which has been heated to the reacting temperature, in general, about 900 to 1,100° C. Nitrogen reacts with carbide to form calcium cyanamide and carbon, essentially as shown by the equation:

$$CaC_2 + N_2 = CaCN_2 + C + 97{,}800 \text{ cals.}$$

The nitrification reaction is not fully understood despite the fact that the process has been operated since 1906 and that numerous investigations on it have been made. From the information available it appears that in the average cyanamide plant not over 80 to 85 per cent of the carbide charged into the nitrifying ovens is converted into calcium cyanamide. The balance of the carbide is very largely destroyed, since only a small percentage is usually found in the nitrified product. The cause of this loss and whether it occurs directly or indirectly, by decomposition of calcium cyanamide, is not known. The presence of oxygen, carbon, dioxide, carbon monoxide, or water vapor in the nitrogen will cause decomposition of calcium carbide and cyanamide, but it has been observed to occur even with pure nitrogen, thus indicating that some other factor—perhaps temperature—is responsible for it.

An excessive temperature in the nitrifying material is to be avoided since the reversibility of the reaction becomes appreciable above about 1,360° C., forming calcium carbide and liberating nitrogen.

The importance of increasing the efficiency of this step as a means of reducing the cost of fixing nitrogen by this process becomes evident when it is remembered that practically the entire cost of the process—perhaps 95 per cent—is for materials, power, labor, etc., up to and including nitrification.

It will be observed that unlike the reaction for the formation of carbide, the nitrification reaction results in the liberation of heat. The heat thus produced is utilized to maintain the carbide charge at the reacting temperature. In properly constructed ovens it is only necessary to supply sufficient heat to start the reaction in a portion of the charge.

The rate of the nitrification reactions is dependent not only on the temperature but on the composition of the charge as well. Moissan[10] found in 1894 that pure calcium carbide would not react with nitrogen at temperatures up to 1,200° C. Frank and Caro, however, used commercial calcium carbide in their preliminary experiments, and it was then established that nitrogen could be fixed in this manner at temperatures considerably below 1,200° C. The rate of nitrification even at temperatures around 1,100° C. was so slow, however, that a large amount of energy had to be supplied to the then rather poorly designed ovens to maintain the charge at the reacting temperature.

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[10] Compt. Rend., 118, 501 (1894).

This objectionable feature of the process was overcome by the discovery that the addition of certain substances, such as alkali and alkaline earth salts, to the carbide resulted not only in increasing very greatly the rate of the reaction but at the same time reducing the operating temperature.

The beneficial effects of adding calcium chloride, in particular, was pointed out by Polzenius, and a cyanamide plant was operated at Westeregeln from 1906 to 1910 under patents covering the use of this salt. It was found, for example, that a carbide containing 10 per cent of calcium chloride would take up in 12 to 14 hours at 730° C. as much as 18 per cent of nitrogen—the theoretical quantity being 22 per cent—whereas carbide alone took up less than 1 per cent under the same conditions.

The presence of calcium chloride in the nitrified product is objectionable, since it absorbs moisture and thus hastens the formation of dicyanodiamide. The latter is to be avoided in cyanamide which is to be used as fertilizer, because of its well-known deleterious action on plant growth. The use of calcium chloride as a catalyst for the nitrification reaction has now been discontinued.

Among other materials which have been used as catalysts for the nitrification reaction, calcium fluoride is perhaps the most important. Its use for this purpose was proposed in 1906 by F. Carlson, and later patented. While the temperature of the reaction is not lowered as much as by the chloride, it has been found that as little as 2 per cent of the fluoride suffices when intimately mixed with the carbide. Moreover, it is not objectionable in the final product, and it is said to have less action on the furnace lining than the chloride. From the information available it appears that calcium fluoride, fluorspar, is now quite generally used.

Although a number of theories as to the nature of the catalytic effect of various added substances on the nitrification reaction have been proposed, none of them appear to be entirely consistent with the observed facts.

There are now two general types of ovens in use for the nitrification of carbide. These are known as continuous and discontinuous ovens. The latter is perhaps the more common one, and is the type installed at United States Nitrate Plant No. 2. Since the ovens at this plant are quite typical of the discontinuous type, they will be briefly described, together with the method of operation.

The ovens are cylindrical in shape and consist of an outer steel shell supported on a reinforced concrete disk. The shell is lined with 5 inches of infusorial earth and 5 inches of fire brick, leaving an oven cavity of about 3 feet in diameter and 5 feet in depth. The bottom is covered with sil-o-cel, over which is placed fire brick. The over has a double cover; the inner one consists of a hollow iron disk filled with infusorial earth, and having a 5-inch opening in the center; the outer one is of sheet steel, belled to form a sand seal on the top of the furnace. Nitrogen is admitted to the oven through the bottom and also through the side near the bottom. A carbon heating pencil or rod placed in the center of the oven serves to bring the carbide adjacent to it up to the reacting temperature.

The finely ground carbide is placed in a heavy paper cylinder a few inches smaller in diameter than the oven. There is also a small paper tube surrounding the pencil so that the charge is held between the two concentric cylinders. After charging, the two covers are placed in position, the carbon pencil inserted, the nitrogen turned on, and current passed through the pencil to heat the charge. The paper tube surrounding the pencil is quickly destroyed, and the carbide adjacent to it soon reaches the temperature of nitrification. The outer paper clyinder is also destroyed after several hours. It is only necessary to continue the heating until the reaction is well started, generally a few hours only. The nitrification, thus started in the core of the cylinder of carbide, proceeds gradually outward until the entire charge is nitrified.

The time required for nitrification depends on the composition and physical condition of the charge, dimensions of the ovens, etc., but it usually ranges from 24 to 40 hours. At the end of this time the nitrified product, which is a grayish-black, solidly caked mass containing about 21 per cent of nitrogen, is removed from the oven to cool.

The ovens at United States Nitrate Plant No. 2 each have a capacity of about 1,600 pounds of carbide per charge. It is understood that very much larger ones have been installed by the American Cyanamid Co. at their plant at Niagara Falls, Canada.

The development of the so-called continuous ovens has been along two somewhat distinct lines. In one of these the carbide, placed in metal boxes, is moved through a long tunnel which is heated and kept filled with nitrogen.

The cyanamide plant at Knapsack, Germany, has nitrifying ovens of this type. The carbide is contained in sheet metal, collapsible boxes of about 3 cubic feet capacity. About 15 of these boxes are placed on an iron car which runs upon a track through the tunnel oven. As the car of carbide enters at one end it pushes forward those already in the oven and the leading car issues from the far end. The ends of the oven are closed by heavy iron doors which are opened only for admittance or withdrawal of the cars, thus excluding air as much as possible. The oven is heated by producer gas burned under the first third of its length, and the nitrogen is admitted at the far end and flows countercurrent to the travel of the cars. These ovens are said to have a capacity of about 27 short tons per 24 hours.

It is understood that difficulties were encountered with such equipment in that the carbide boxes were badly deformed by heat and had to be reworked very frequently; the doors of the ovens warped badly, and, moreover, they were open for the considerable time which was required in putting in or taking out the cars; and apparently the product was much less uniform than from other types of ovens.

A somewhat similar oven is used at the cyanamide plant at Marignac, France. In this case the carbide, also contained in metal boxes, is moved through a long, nitrogen-filled tunnel without the use of cars. The carbide is given a certain amount of agitation by a combined longitudinal and vertical movement of a section of the floor by means of suitable cams. The oven is heated by carbon pencils which extend from side to side just under the ceiling and a short distance above the carbide. These pencils are spaced more closely near the entrance of the furnace than elsewhere to provide the necessary heat during the early part of the reaction. Loss of nitrogen and dilution by air are minimized by the use of caisson trapdoors. These ovens have a capacity of 25 to 40 tons of cyanamide per day, and appear to have a number of advantages over those at Knapsack.

A more nearly continuous nitrifying oven has been developed in Sweden by the Carlson company and has been in successful operation in that country for a number of years. These ovens are cylindrical, towerlike structures, containing shelves so arranged that the carbide, charged in at the top, is caused to move downward from shelf to shelf by means of a mechanical scraper. The nitrogen is admitted at the bottom of the oven. The heat required to start the reaction is furnished by arcs near the top of the furnace. The nitrified carbide is discharged at the lower end. It is stated that the temperature in the oven is about 950° C.; that approximately two hours are required for the passage of the carbide through the oven; that the product is obtained in the form of lumps about three-fourths inch or less in diameter which can be easily ground; and that it contains about 21 per cent of nitrogen. It appears that the difficulty encountered in early attempts with this type of oven due to caking has been successfully overcome in this oven.

The advantages claimed for the continuous oven over the discontinuous type are[11] a lower capital cost, a lower consumption of carbide per ton of nitrogen fixed, a lower consumption of energy, and a lower operating and maintenance charge. Such an economy in carbide utilization would, as previously mentioned, be very important. It seems to be an open question, however, whether the continuous ovens are better than the modern very large capacity discontinuous ovens.

The efficiency of the nitrification reaction with respect to nitrogen appears to be quite low for all types of ovens. For example, in the discontinuous type as generally operated less than half of the nitrogen entering the oven is actually fixed. With more careful regulation, however, it seems probable that 60 to 70 per cent of the nitrogen could be fixed. No definite figures are available on the nitrogen requirement of continuous ovens. It should be pointed out in this connection, however, that the cost of nitrogen is a relatively small item and consequently a relatively low efficiency is not particularly serious.

The composition of the nitrified carbide will vary considerably in the different countries, since it depends on the quality of raw materials, on carbide furnace practice, and on the method of nitrification. In general, however, the nitrogen content ranges from 19 to 22 per cent. The principal constituents of the cyanamide produced at United States Nitrate Plant No. 2 are shown in the following:

	Per cent.
Calcium cyanamide	61.2
Calcium oxide	20.0
Calcium carbide	1.5
Calcium sulphide	0.2
Calcium phosphide	0.04
Free carbon	12.5
Silica	2.4
Iron and aluminum oxides	1.8
Magnesium oxide	0.2

h. Crushing and milling of calcium cyanamide.—The presence of unnitrified carbide in the cyanamide is objectionable both in the production of ammonia by autoclaving and in the material which is to be used as fertilizer, as will be discussed later. The only practical method of destroying the carbide appears to be to finely grind the cyanamide and then treat it with a spray of water.

The type of crushing and grinding equipment will depend somewhat upon the type of nitrifying oven used. Cyanamide produced in discontinuous ovens is in the form of solid cakes similar to carbide, but much less hard, and consequently requires similar crushers and mills. In fact, at United States Nitrate Plant No. 2 the same kind of equipment is used for the two materials. Of the final product, 65 to 70 per cent passes through a 200-mesh screen.

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[11] Final report Nitrogen Products Committee, p. 258.

It is understood that grinding calcium cyanamide to this degree of fineness is, as a rule, not practiced in many of the European plants. It appears to be quite necessary, however, for the complete elimination of carbide.

i. Treatment of calcium cyanamide for use as fertilizer.—The principal necessity for the treatment of raw cyanamide before this material can be used as fertilizer arises from the fact that it frequently contains as much as 1.5 to 2 per cent of unnitrified carbide. The storage and transportation of such material is attended by considerable risk of acetylene explosion unless packed in air-tight containers.

The elimination of the carbide by fine grinding and spraying with water—previously referred to—results in an exceedingly dusty product whose handling is very disagreeable. The lime and calcium cyanamide dust attacks the skin to a certain extent, and cyanamide itself is specifically somewhat toxic to human beings.

The treatment of the material with sufficient water to hydrate the free lime is also desirable, since unhydrated material when bagged absorbs moisture and carbon dioxide from the air, resulting in an increase in volume and the consequent bursting of the bags.

A large number of methods of treating cyanamide have been proposed. These fall in two general groups—granulation and hydrating and oiling.

Under granulation may be mentioned the process of crushing the raw cyanamide to a size which is suitable for direct application to the soil. Any fine material produced in the crushing is converted into ammonia by autoclaving. It is understood that a part of the cyanamide marketed as fertilizer in France since the war is in this form. This granular cyanamide contains carbide and is consequently open to objections for that reason.

Another method of granulation which has been used to a considerable extent consists in treating the powdered cyanamide with water alone or with water containing a so-called binder, forming the material into granules by means of pressure, and then drying. Such methods invariably result in the formation of prohibitive amounts of dicyanodiamide. The harmful action of this material on plant growth is well known, and many of the poor results obtained with granulated cyanamide can be safely ascribed to its presence. This method of treating cyanamide has been practically discontinued.

The second method of treating cyanamide—hydrating and oiling—appears to be the most satisfactory solution of the problem, and the operation is an inexpensive one. In this process the finely ground cyanamide is treated with sufficient water, in the form of a fine spray, to destroy the carbide and hydrate the free lime. Between 6 and 7 per cent of water is usually required for this purpose. An excess of water is to be avoided since it would result in the formation of dicyanodiamide. Hydration with this quantity of water does not appreciably reduce the dustiness, and therefore the material is treated with 3 to 4 per cent of oil in the form of a spray. A cheap grade of mineral oil is generally used, although other kinds of oil could be employed.

The hydration of raw cyanamide results in the liberation of a large amount of heat; and since high temperatures and the presence of moisture furnish favorable conditions for the formation of dicyanodiamide, the process must be carefully carried out. Exceedingly thorough agitation of the material while the water and oil is being introduced is absolutely essential for satisfactory treatment. When properly carried out, the loss of nitrogen as ammonia is negligible and very little, if any, dicyanodiamide is formed. No standardized form of equipment has been developed for hydrating and oiling cyanamide, but it appears probable that some adaptation of a cut-flight conveyor would be quite suitable.

The stability of hydrated and oiled cyanamide during storage is very largely dependent on the conditions of exposure. There is in all cases a tendency for the transformation of cyanamide into dicyanodiamide to occur, but the rate of this reaction will depend on the accessibility of the cyanamide to atmospheric moisture and carbon dioxide, and also on the temperature. Obviously the deterioration will be faster in rather porous bags than in more impervious ones, and faster in bagged material than in bulk.

Cyanamide fertilizer is generally handled in double burlap bags, and when properly hydrated and oiled it can be kept for six months to a year under ordinary conditions of fertilizer storage without danger of deterioration.

The great advantage of cyanamide is its cheapness. However, it has several disadvantages which at the present time overbalance this advantage and prevent its general use as a fertilizer. These disadvantages are: (1) It is a very disagreeable substance to work with and is somewhat toxic to human beings if large amounts of the material get into the skin; (2) it can not be used in large quantities in mixed fertilizer containing acid phosphate owing to the mutual reaction between the acid phosphate and the cyanamide which causes the acid phosphate to revert and also may lead to the formation of the agriculturally undesirable substance, dicyanodiamide; and (3) it has an inherent toxicity to plant growth greater than that of other fertilizer materials, which prevents its use in as large quantities as other forms of nitrogen-containing substances, a factor which is particularly noticeable in dry seasons. On the other hand, it can be successfully mixed with basic phosphate and with calcined phosphate in a manner so that no harmful reactions take place between the phosphate and the nitrogen-containing materials.

j. Production of ammonia from cyanamide.—The production of ammonia from cyanamide is a simple and comparatively inexpensive operation, consisting in the treatment of cyanamide with water and steam in an autoclave. It is very largely for this reason that the cyanamide process has assumed its present important position as a method of fixing nitrogen, since a very large part of the cyanamide produced is utilized in this manner.

The process was patented by A. Frank in Germany in 1900 (D. R. P. 134,289) and in this country in 1904 (U. S. 776,314). It is now in commercial operation in many countries, since the increasing use of cyanamide for the production of ammonia, particularly during the war, has resulted in the installation of autoclaving equipment at the majority of cyanamide plants. The autoclaving process has been quite fully described by Landis.[12]

The process as actually carried out consists in the following steps: The elimination of free carbide by hydration; the treatment of the hydrated cyanamide with water and steam in an autoclave; the separation of ammonia from the steam-ammonia mixture; the treatment and disposal of the autoclave sludge.

To obtain the ammonia gas as free from acetylene as possible, the finely ground cyanamide is first treated to destroy substantially all of the free carbide. This is accomplished by spraying the material with a quantity of water, corresponding to about 2 per cent of the weight of the cyanamide, while it is being agitated in a mixing and conveying trough.

The cyanamide nitrogen is then converted into ammonia by autoclaving with an approximately 3 per cent sodium hydroxide solution in the proportions of about 1 to 2.4, at temperatures considerably above 100° C. The net result of the chemical changes involved in the treatment of calcium cyanamide with water are quite accurately represented by the equation:

$$CaCN_2+3H_2O=2NH_3+CaCO_3.$$

The actual course of the reaction is not fully understood, but it is known to be quite complicated. The liberation of nitrogen as ammonia can, however, be made practically quantitative on a commercial scale. It has been found that the presence of alkali greatly facilitates the conversion reaction, presumably by preventing to a large extent the formation of the more difficultly decomposable nitrogen compounds, and by assisting in the decomposition of those compounds when formed.

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[12] Chem. and Met. Eng. 14, 87 (1916).

The formation of ammonia from cyanamide is accompanied by the liberation of heat, so that once the reaction is started it proceeds very vigorously, causing the pressure in the autoclave to increase very rapidly.

A brief description of the autoclave equipment and method of operation at United States Nitrate Plant No. 2 will serve to illustrate the process. The autoclaves are steel tanks 21 feet high, 6 feet in diameter, with 1¼-inch wall thickness, and constructed to operate at pressure up to 300 pounds per square inch. They are provided with stirrers consisting of a central vertical shaft carrying three sets of arms and also a drag on the bottom.

In operating these autoclaves about 19,000 pounds of filtrate liquor from a previous operation are introduced and then 8,000 pounds of cyanamide. A sufficient quantity of soda ash—usually 150 to 300 pounds—is added to give a concentration of alkali equivalent to about 3 per cent sodium hydroxide. The charge is aerated for 10 to 15 minutes to eliminate acetylene, phosphine, and hydrogen sulphide as completely as possible. The autoclave is then closed and the reaction started by introduction of steam at the bottom until the pressure reaches 60 pounds. The reaction then proceeds rapidly of its own accord, and ammonia, accompanied by large volumes of steam, is continuously discharged from the autoclave. About 85 to 90 per cent of the nitrogen is converted into ammonia and discharged by the time the reaction subsides, with consequent drop in pressure to 1 atmosphere. To obtain a practically complete conversion the autoclave is again closed and the charge subjected to the action of steam at about 120 pounds pressure for two hours. The ammonia is then discharged and any gas remaining dissolved in the liquor is driven out by the introduction of steam for a short period. The complete cycle of operations per charge generally requires from five to six hours. During the test run at United States Nitrate Plant No. 2 about 97 per cent of the total nitrogen in the cyanamide was obtained as ammonia.

The ammonia discharged from the autoclaves is accomplished by a very large quantity of steam, perhaps averaging for the entire discharge about three times the weight of ammonia. A certain amount of suspended solids is also carried out and is removed by means of a mud drum. Although the ammonia-steam mixture can be used directly in the manufacture of ammonium sulphate, it is preferable or necessary in many cases to obtain rather dry gas. This is accomplished by treatment of the mixture in an ammonia still provided with suitable condensers. The construction and operation of such equipment has been so fully described by Lunge[13] and others that it will not be treated in this report.

The slurry discharged from the autoclaves is filtered to recover the alkali for reuse in the process. The filter cake contains about 40 per cent of water and on the dry basis has approximately the following composition: Calcium carbonate, 63 per cent; calcium hydrooxide, 22 per cent; graphite, 10 per cent; iron and aluminum oxides, silica, etc., 5 per cent; and generally less than 0.2 per cent of nitrogen.

The disposal of the filter cake from a large conversion plant is seen to be a very large problem when it is considered that about 5 tons of cake, on the dry basis, are produced per ton of ammonia, corresponding to 8 to 9 tons of wet cake as actually obtained.

Various suggestions have been made as to the utilization of this material, but no satisfactory solution of the problem has as yet been obtained. It has been proposed, for example, to use it as agricultural lime, in carbide manufacture, in cement manufacture, and as a source of graphite through chemical or electrical separation methods.

There appears to be no valid objection to its use as agricultural lime, but the output from even a medium-sized plant is so large that, in general, any local demand would be greatly exceeded, and the material can only stand a very small freight charge.

Its use in carbide manufacture does not appear to be commercially feasible, at least at the present time, since drying, calcining, and briquetting would be necessary. Moreover, there would be a gradual accumulation of impurities from the additional coke required, from the fuel used in calcining—unless gas were used—and also from the catalyst, if used. Some of these difficulties would also be encountered in using it for cement manufacture. Attempts at separation of the graphite for use in electrode manufacture or other purposes by chemical, flotation, or electrostatic means have not thus far proven to be economically successful.

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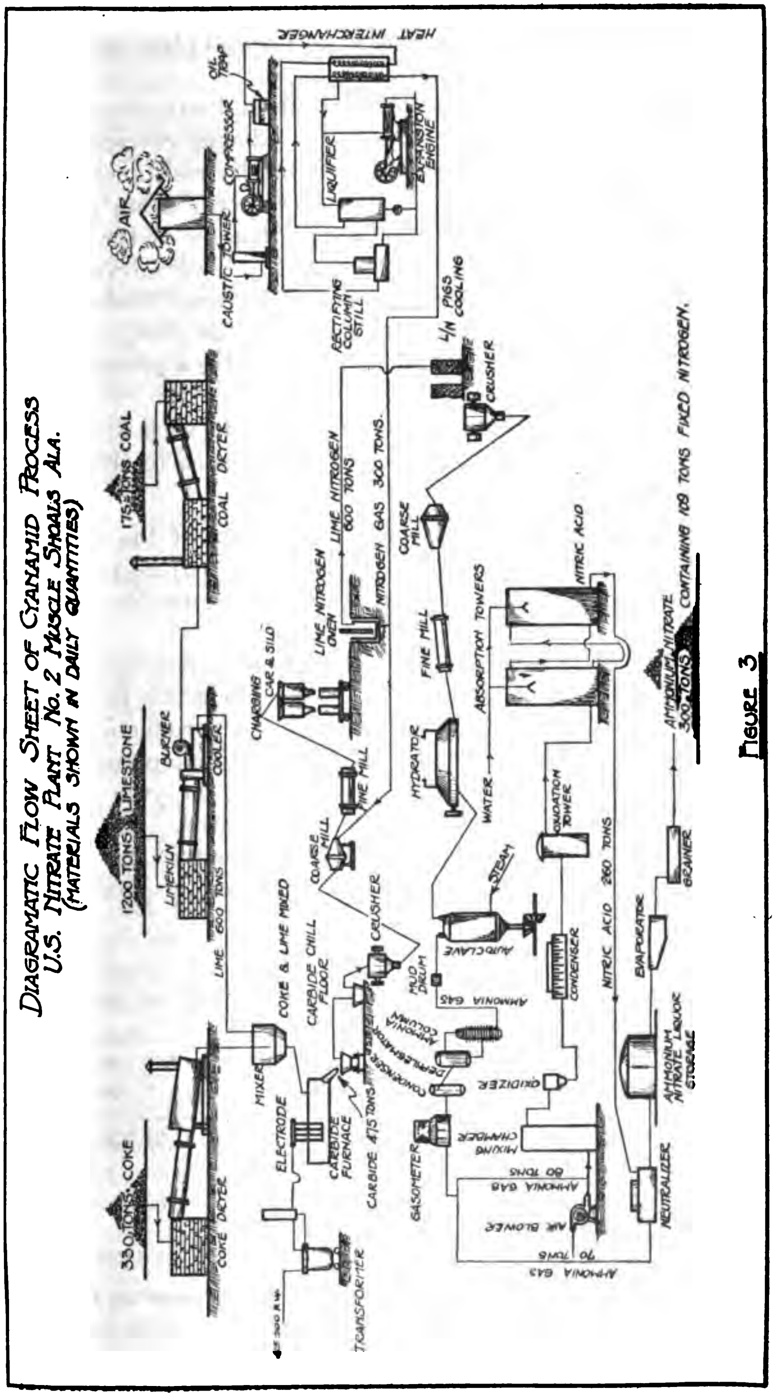
[13] Coal Tar and Ammonia, Pt. III, 5th ed., p. 1342 (1916).



DIAGRAMATIC FLOW SHEET OF CYANAMID PROCESS
U.S. NITRATE PLANT No. 2 MUSCLE SHOALS ALA.
(MATERIALS SHOWN IN DAILY QUANTITIES)

FIGURE 3

2. Modification of Cyanamide Process.

A modification of the standard cyanamide process has been proposed by James H. Reid, and a small experimental plant for its operation has been built at Sherman, Vt.

Briefly, the process consists in coking a ground mixture of coal and limestone in a retort, with gas recovery; producing carbide from the suitably crushed, coked material in an essentially resistance-type furnace; and nitrifying the carbide thus produced, using previously nitrified carbide as a catalyst. The unique feature of the process is the coking of limestone and coal *together.* Two advantages are claimed for it: The coked material is an electrical conductor, and hence can be used in a furnace operating on the charge-as-resistor principle, and the limestone acts as cracker to give a greater yield of gas than in coking coal alone.

The process has as yet not been developed to such a stage that conclusions as to its commercial feasibility can be correctly drawn.

3. Construction and Operating Costs.

In discussing construction and operating costs of the cyanamide process, the United States Nitrate Plant No. 2 will be used as the working basis, as rather complete and accurate figures on this plant are available.

The cost of that part of plant No. 2 up to and including the production of cyanamide and including the steam-electric power plant was $33,500,000, while that portion through the production of ammonia gas was $4,000,000 more, or $37,500,000. This plant was constructed as a war emergency during war times, the year 1918, and so was affected by rising labor and materials costs. Reproduction at this time will therefore be taken at 60 per cent of the war cost, which will make the cost of a cyanamide plant for the production of commercial materials as follows:

Plant for cyanamide.

(Capacity, 245,000 tons commercial cyanamide fertilizer (19.3 per cent N) per year.)

Sixty per cent of $33,500,000	$20,100,000
Extra for oiling and hydrating equipment	1,250,000
Cost of plant	21,350,000

Or $90 per annual ton of commercial cyanamide.

Plant for ammonia gas.

(Capacity, 55,250 tons per year.)

Sixty per cent of $37,500,000=$22,500,000 cost of plant, or $410 per annual ton of ammonia gas.

Plant for sulphate of ammonia.

(Capacity, 215,000 tons per year.)

Sixty per cent of $37,500,000	$22,500,000
Extra for sulphate plant equipment	3,000,000
Cost of plant	25,500,000

Or $120 per annual ton of sulphate of ammonia.

The direct synthetic process ordinarily has an operating advantage in that its power costs as compared with those of the cyanamide process are very small. This advantage disappears in the particular instance of United States Nitrate Plant No. 2 with the possibility of 2-mill hydroelectric power.

In the study of operating costs power, except where otherwise noted, is taken at 4 mills per kw.-hr. Costs of actual production of the various products are estimated in detail in Appendix C, and the results obtained there will be used here. It is to be noted that interest on working capital is not included in the estimates of this chapter. Production costs in the case of commercial cyanamide and sulphate of ammonia include an estimate for handling, sales, research, and main office, while for ammonia this figure must be added.

Cost of ammonia (per ton).

Production cost	$137.30
Estimate for handling, sales, research, and main office	12.50
Interest, depreciation, obsolescence, insurance, and taxes, at 15 per cent of $410	61.50
Cost per ton	211.30

Or 10.6 cents per pound.

With 2-mill power this cost would be reduced $22.88 per ton, making the cost 9.5 cents per pound. In this estimate no allowance has been made for royalty payments on processes which, in the case of United States Nitrate Plant No. 2, would amount to $27.02 per ton of ammonia, making the cost with 4-mill power 11.9 cents per pound of ammonia and with 2-mill power 10.8 cents per pound of ammonia.

Cost of sulphate of ammonia (per ton).

Production cost	$53.36
Interest, depreciation, obsolescence, insurance, and taxes, at 15 per cent of $120	18.00
Cost per ton	71.36

If 2-mill power is secured this cost will be reduced by $5.88, making the cost of the material $65.48 per ton.

No allowance has been made in this estimate for cost of patents which, in the case of United States Nitrate Plant No. 2, amounts to

$6.77 per ton of sulphate, increasing costs to $78.13 for 4-mill power and $72.25 for 2-mill power.

The average pre-war price was $60 per ton.

Cost of commercial cyanamide (per ton).

Production cost	$32.87
Interest, depreciation, obsolescence, insurance, and taxes, at 15 per cent of $90	13.50
Cost per ton	46.37

This material contains 19.3 per cent nitrogen, equivalent to 23½ per cent ammonia, and, using the above cost figure, has a cost equivalent of $1.97 per unit of ammonia. The average pre-war price was $2.12 per unit of ammonia.

In this estimate no allowance has been made for cost of patents which, in the case of United States Nitrate Plant No. 2, would be $6.28 per ton of material, increasing the price equivalent to $2.24 per unit of ammonia.

With 2-mill power the cost would be reduced $5.10 per ton, or $41.27 without royalties and $47.55 with the royalty in effect in the case of United States Nitrate Plant No. 2, giving a price equivalent in the first case of $1.76 per unit of ammonia and in the latter of $2.02 per unit of ammonia.

B. THE DIRECT SYNTHETIC AMMONIA PROCESS.

1. History of Process.

Prof. Fritz Haber, of Karlsruhe, Germany, after much careful experimental work[14], patented[15] a process whereby nitrogen and hydrogen in the presence of a reaction promoter combined directly to form ammonia, according to the equation $N_2+3H_2=2NH_3$. This is the basis of what has become known as the Haber synthetic ammonia process. Although Haber is given credit for the invention of the process, many others carried out investigations on the subject prior to those of Haber. Nernst was the first to have had success with an apparatus to operate under the unusual conditions of high temperature and considerable pressure. Nernst and the others, however, did not have the good fortune to find an effective catalyst, while Haber did. Nernst quickly lost interest in the work, while Haber was encouraged and continued energetically in an effort to apply the process industrially.

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[14] F. Haber and R. Le Rossignel, Ber. 40 (1907), 2144; Z. Elektrochem., 14 (1908), 181; ibid., 19 (1913), 53; F. Haber, Chem. Ztg., 34 (1910), 345; Z. Elektrochem., 16 (1910), 244; F. Haber et al., ibid., 20 (1914), 597; ibid., 21 (1916), 191.

[15] Haber, D. R. P. 229,126 (1909); 238,450 (1909); Haber and Le Rossignel, U. S. patents 971,501 (1910); 999,025 (1911); 1,006,206 (1911); 1,202,995 (1916); Badische Anilin und Soda Fabrik, D. R. P. 235,421 (1908); 259,996 (1911).

There are to-day in general four definite developments of the Haber process for the direct synthesis of ammonia: The original German (Haber), the American (General Chemical Co.), the French (Claude), and the Italian (Casale). The conditions necessary in all of these processes to bring about an appreciable combination of hydrogen with nitrogen, even in the presence of the best reaction promoters or catalysts so far developed, involve pressures of over 100 atmospheres, and temperatures of 450° C. to 600° C. The concentration of ammonia thus obtained in the nitrogen-hydrogen mixture, according to present industrial practice, is of the order of 5 to 10 per cent. The four developments are fundamentally similar, differing essentially in the operating pressures (100 to 1,000 atmospheres) used for synthesis and in the methods for removal of ammonia from the gases (liquefaction by cooling and absorption). There are in all of the processes the mechanical difficulties attendant to operation under combined high temperatures and high gas pressures, and there is the need of an active, rugged, cheap catalyst which will operate at as low temperatures as possible. There are two principal methods used to produce the raw gases for the process, the Bosch water gas and the water electrolysis.

The German process developed by Haber uses a pressure of about 200 atmospheres, and the catalysis temperature is about 500° C. The synthesis takes place in a circulating system from which the ammonia is removed by water absorption. The units employed in the German commercial installation are of large capacity, each catalyst bomb synthesizing about 15 tons of ammonia per day.

The American process was developed by the General Chemical Co. and involves pressures of approximately 100 atmospheres. The low pressure utilized in this process was made possible by the activity of the catalyst developed by the General Chemical Co. The greater the activity of a catalyst, however, the greater is its sensitiveness to poisons in the gases. It is therefore necessary that great precaution be taken in the purification of the gases. The synthesis takes place, in this process also, in a circulating system from which the removal of ammonia is accomplished by refrigeration and liquefaction at extremely low temperature (—40° C.), the low temperature being necessary in view of the small concentration of ammonia obtained at the comparatively low pressure of 100 atmospheres. Commercial units have been built with rated capacities of 5 to 10 tons of ammonia per day each.

The French process as developed by Claude uses pressures of 600 to 1,000 atmospheres at temperatures somewhat higher than those used by the Americans and Germans. Catalysts are more active and less affected by poisons in the gases at the higher operating temperatures. Claude consequently can obtain satisfactory results with catalysts inferior to those required for the lower pressures. The ammonia is removed by cooling the gases to the point of liquefaction of the ammonia, the liquid being discharged from the system. Very low temperature cooling for liquefaction of ammonia is not necessary on account of the higher pressures used, the liquefaction temperature being approximately 20° C. Also, due to the high pressures and with a comparatively poor catalyst, the concentration of ammonia rises to more than 20 per cent. With such large ammonia concentrations, a circulating system may not be used, the gases being passed through several reaction chambers in series and the ammonia removed at the exit of each, while the residual gas from the last of the chambers will be rejected. A combination of series and circulating systems is being used, however, in the latest development for operation under these pressures. The gases are passed from the high-stage compressor through two converters in series, ammonia being removed at the exit of each, while the gas from the second one is returned to an intermediate stage of the compressor, where it is mixed with fresh gas and returned to the converters. The upper stages of the compressors, therefore, function also as circulating compressors. The individual units for operating pressures of 600 to 1,000 atmospheres are quite small as compared to those operating at the lower pressure of 100 to 200 atmospheres. The installation built by Claude in France has progressed only to a semicommercial stage, its capacity being from 1 to 2 tons of ammonia per day.

The Italian process was developed by Casale and operates at pressures of 300 to 600 atmospheres. The synthesis takes place in a circulating system from which the ammonia is removed by liquefaction due to cooling. The Italians claim to have a catalyst which is free from deleterious action of poisons in the gases. The units employed so far have a capacity of less than half a ton per day.

England is developing the direct synthetic ammonia process essentially, according to the principles of the German Haber, and is now building a plant of about 10 tons per day capacity.

The Japanese have acquired rights to the American process and are negotiating with the Germans and French, but have as yet constructed no plants.

The nitrogen and hydrogen necessary for the ammonia synthesis may be obtained by any of several commercial methods, the more important of which are the Bosch process as developed in the German Haber-Bosch plants where water gas is the intermediate step from water to pure hydrogen; and the electrolytic process, where hydrogen is obtained directly by the electrolytic decomposition of water. The complete German synthetic process, including the manufacture of the gases, is more properly known as the Haber-Bosch process, crediting the development of the methods of manufacture and purification of the gases to Dr. C. Bosch, of the Badische Anilin und Soda Fabrik, of Ludwigshafen, Germany. The Bosch method for gas manufacture and purification has been used in the German and American plants and is to be used in the English plant now being constructed. This method involves the production of water gas and its further reaction with an admixture of steam in the presence of a catalyst according to the equation.[16]

$$CO+H_2O=CO_2+H_2.$$

The nitrogen may be obtained in the mixture by injection of air during the manufacture or oxidation of the water gas, or by the production of a pure producer gas to be mixed with the water gas before oxidation [17] [18]. The gas mixture after oxidation contains, besides nitrogen and hydrogen, large quantities of carbon dioxide with some carbon monoxide. Extensive purification is necessary [17], [19], [20], the carbon dioxide being removed by water washing at high pressure, the carbon monoxide by scrubbing with cuprous solutions and incidental impurities by various special means. The purified gas, approximately 3 parts hydrogen and 1 part nitrogen, is then available for ammonia synthesis.

Hydrogen of high purity for the synthetic process can be manufactured by the electrolytic decomposition of water. This method is limited to those localities in which very cheap power may be obtained, as, for instance, from large water-power developments or where low rates may be obtained for off-peak power or where the hydrogen is a by-product of oxygen or chlorine manufacture. The Italians and the French use this method in their comparatively small plants. Nitrogen of high purity made by the liquid-air process may be added to the hydrogen; or, if the electrolytic hydrogen is sufficiently cheap, the nitrogen may be added as air, the oxygen being burned out with excess hydrogen. The electrolytic production of hydrogen for the synthetic process is considerably more simple mechanically than the Bosch method of production, because the most difficult steps in the purification of the gases are eliminated, while the manufacture of the gas itself is a very simple and standardized process.

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[16] B. A. S. F. (C. Bosch), U. S. patent 1,102,716 (1914); Brit. patent 26,770 (1912); Fr. patent 459,918 (1913); General Chemical Co. (de Jahn), Brit. patent 124,760 (1918).

[17] H. C. Greenwood: Industrial Gases (Balliere, Tindall & Cox) (1920).

[18] B. A. S. F., Brit. patent 27,117 (1912); (C. Bosch) U. S. patent 1,115,776 (1914); (C. Bosch) U. S. patent 1,200,805 (1916).

[19] General Chemical Co. (de Jahn), Brit. patent 120,546 (1918).

[20] Vignon, Fr. patent 389,671 (1908); B. A. S. F., D. R. P. 282,505 (1913); Brit. patents 8,030 (1914); 9,271 (1914); U. S. patent 1,196,101 (1916); D. R. P. 289,106 (1914); General Chemical Co. (de Jahn), Brit. patent 120,546 (1918).

A description of the direct synthetic-ammonia process follows, giving a brief discussion of apparatus and operating conditions for each step.

2. Description of Process.

a. Production of raw gases.—Water-gas manufacture: The water-gas process, with standard equipment, consisting of gas generators, wash boxes, and gasometers, as used in the manufacture of illuminating gas, may be employed to decompose steam for the production of free hydrogen and oxides of carbon. In a subsequent paragraph it is shown how the carbon monoxide of this gas is utilized for the production of more hydrogen and how the carbon dioxide is removed. The approximate composition of the water gas is given in Table I, and it will be noted that 100 volumes of this mixture contain approximately 50 volumes of hydrogen as such and 40 volumes of potential hydrogen (later available when carbon monoxide combines with steam), making a total of 90 volumes of hydrogen. It may be noted that a high nitrogen content in the gas is not objectionable for this process, since there is later an admixture of either pure nitrogen gas or gas of high nitrogen content. Hence steps may be taken to decrease the loss of hydrogen in the stack, even though nitrogen be added to the gas. The gases are passed through standard wash boxes and water scrubbers, but on account of purification in a later stage of the process no special purifiers are required before the gases are passed into the storage holders.

TABLE I.—*Water-gas composition.*

	Operating ranges.	
	Per cent.	*Per cent.*
CO_2	5 to 3	5 to 3
CO	42 to 45	41 to 44
H_2	51 to 50	49 to 48
N_2	2 to	5
Total	100 to 100	100 to 100

Producer-gas manufacture: Standard methods for the manufacture of lean or producer gas may be employed to secure a gas mixture rich in nitrogen and lean in hydrogen. Oxides of carbon are also present in lean gas; and since some steam is used with the air, hydrogen also is present. Inasmuch as the producer gas, as the main source of nitrogen, may be later added to the water gas, the hydrogen in the former, as well as the carbon monoxide, as potential hydrogen, becomes available. The producer gas may have the composition shown in Table II. The range of composition is wide, depending on the nature of the fuel and the operating conditions. One hundred volumes of producer gas represent approximately 60 vol-

DIAGRAMATIC FLOW SHEET OF DIRECT SYNTHETIC AMMONIA PROCESS
DIAGRAM OF AMERICAN MODIFICATION OF HABER PROCESS AT
U.S. NITRATE PLANT No. 1 SHEFFIELD, ALA.

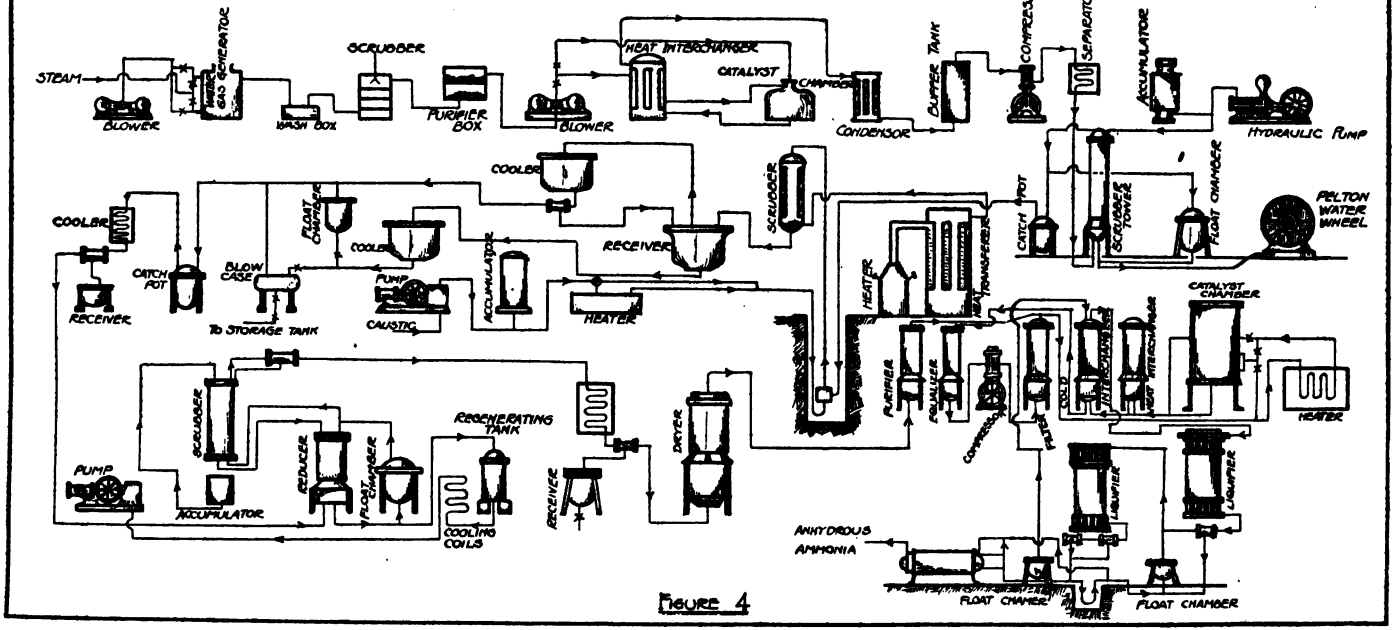

FIGURE 4

umes of nitrogen and 30 volumes of hydrogen as such, or as potential hydrogen.

TABLE II.—*Producer-gas composition.*

	Per cent.
H_2	5–15
N_2	65–50
CO	20–30
CO_2, CH_4, etc	5–10

Coke should be used in the manufacture of lean gas, as well as water gas, to keep the methane content as low as possible, since the purge of methane and inert gases from the purified gases is expensive.

Mixing of water and producer gas: To obtain the desired final ratio of 3 parts of hydrogen (actual plus potential) to 1 of nitrogen, a mixture of very nearly 2 volumes of water gas to 1 volume of producer gas of the above composition would be required, and since one generator can make approximately three times as much lean gas by volume as it can water gas, there need be only one lean-gas machine for six water-gas machines. The composition of the mixed gas is, to a great extent, independent of the compositions of the producer and water gases, if we assume that these gases have been mixed in proper proportion to secure the desired final ratio between the hydrogen and nitrogen. The final composition will, in normal practice, vary only within narrow limits and should be as indicated in Table III for both cases when the complete nitrogen requirement is introduced at the gas machines and when gas is made deficient in nitrogen.

TABLE III.—*Mixed-gas composition.*

	Per cent with complete nitrogen.	Per cent with deficient nitrogen
CO_2	3–5	3–5
CO	39–36	41–38
H_2	34–36	37–39
N_2	23–22	18–17
X (CH_4, argon, etc.)	1–1	1–1
Total	100–100	100–100

Water gas, as the principal source of hydrogen, and lean or producer gas, as the principal source of nitrogen, may be delivered to separate holders by exhausters equipped with water injectors for saturating the gas and followed by cyclone separators to remove excess water. The gases may then be passed through meters to a mixing main equipped with turbo blowers to mix the gas. The mixed gases should be so proportioned as to be somewhat deficient in nitrogen, as will later be explained. Mixing of water and producer gases is the method employed in the German plants.

Direct manufacture of mixed gas: In lieu of making the two gases separately and mixing them in the desired proportions, the mixture may be made directly by the introduction of air into the water-gas machine during its "making" period.[17, 19] The use in the direct method of only a part of the blowing air simultaneously with steam during gas production involves many operating difficulties, the most important of which is the variable composition of the effluent gases. All of the air will yield nitrogen and oxides of carbon, but the proportion of steam decomposed, and therefore the resultant proportion of hydrogen produced, will depend upon the grade of fuel used, temperature, and cleanliness of the fuel bed and will vary from the beginning to the end of each "run." Thus the composition of the effluent gases is dependent on too many possible variables in operation. The net result of this direct method is the combining of the water-gas machine and the producer in one apparatus. Operating considerations may definitely determine which of the preceding methods to employ, although a theoretical comparison leads to little choice. Producers can use a lower grade of fuel than water-gas machines, which may be the determining factor in the choice of method, although in small plants duplication of apparatus may be the controlling factor.

Water gas and air burning: It may, in some installations, be necessary to burn air in a later step of the process for purposes of temperature maintenance. The air required for temperature maintenance may in some installations furnish nearly all of the nitrogen necessary for synthesis. It would, therefore, be only necessary in such a case to operate the gas machines for the production of water gas rich in hydrogen. This method of operation, although in some cases it may be necessary, is fundamentally inefficient since air injected into the gas with combustion of the latter involves a definite loss of hydrogen or carbon monoxide (later yielding hydrogen) in the formation of water, whereas the nitrogen available from the gas-generator blast represents no loss of fuel. Complete nitrogen supply by air injection and combustion in the gas involves a loss of 25 per cent of the hydrogen obtainable from a given volume of water gas with nitrogen added as blast gas and thus increases the fuel consumption considerably.

Manufacture of hydrogen electrolytically: Little need be said concerning the actual manufacture of hydrogen electrolytically, since production by that method is a standardized operation. There is, however, a great disadvantage in the electrolytic production of hydrogen for the synthetic ammonia process, since cells as they are now built are comparatively small in capacity (500 to 1,000 amperes);

[17, 19] Loc. cit., p. 99.

and where large volumes of gas are required, such as in an ammonia process, the investment cost for an electrolytic hydrogen installation becomes enormous. One of the leading cell manufacturers in this country has experimentally developed a 10,000-ampere cell, the tests of which were very successful, giving every indication that commercial units of that capacity could be built and operated with no difficulty. It is believed that other companies will follow as quickly as they can convince themselves that the time has come for electrolytic-gas production on a large scale. The large cells of 10,000-amperes rating should be capable of handling an overload of 50 per cent, thus for the same gas production, using the large capacity cells as compared with the present-day standard cells, the ratio of investment costs would be of the order of 1 to 4 in favor of the large cells. The large electrolytic cell therefore warrants serious consideration as a gas producer for the synthetic ammonia process.

The power consumption for electrolytic production of hydrogen is an item of prime importance. While the Bosch method of gas production consumes about 4,000 kilowatt hours per ton of ammonia, the electrolytic method consumes more than four times as much, putting this method as a power consumer in a class with the cyanamide method for ammonia production.

Manufacture of nitrogen: Free nitrogen is necessary, in cases where circulating synthesis systems are employed, to control the final nitrogen-hydrogen gas ratio of 1 to 3 before synthesis, and also for other incidental purposes about the plant. As before stated, the gas ratio is made slightly low in nitrogen at the beginning of the process, because it is impossible to maintain a correct ratio throughout the system up to the point of synthesis, due to variables in purification, and due to the fact that variable amounts of nitrogen in the form of air may be introduced for internal combustion and heat maintenance at different points of the system. It is therefore desirable that free nitrogen be available for introduction just before synthesis to obtain the correct proportions of nitrogen and hydrogen. It is important, in a circulating system, that the correct proportion be obtained, since any excess of either constituent rapidly builds up in the synthesis system.

Any of the standard liquid-air processes, consisting of distillation columns, compressors, etc., are suitable for the production of nitrogen, or, as before stated, if electrolytic hydrogen is cheap, excess hydrogen may be used to burn the oxygen out of the air, leaving the nitrogen for use in the process. The apparatus to produce nitrogen by the latter method would be simple, consisting of a suitable burner to burn air in a hydrogen atmosphere. The water formed would have to be removed as will be discussed later.

b. Oxidation of carbon monoxide, Bosch method.—General description: The mixed gases furnished by the water-gas and producer-gas machines for the Bosch method of gas production contain carbon monoxide, carbon dioxide, and small quantities of other gases along with the desired constituents, nitrogen and hydrogen. It is the purpose, therefore, to remove all but the latter. A step preliminary to the removal of these undesirable gases is the oxidation of the carbon monoxide to produce carbon dioxide and hydrogen.

In general the oxidation of carbon monoxide to dioxide is accomplished in a system as follows: The mixed gases are passed through a series of heat interchangers into a converter. At a point in the path through the interchangers where the temperature is suitable, steam is added to the gases. The mixture then continues into the converter, where, by the aid of a suitable catalyst and at high temperature, the steam reacts with carbon monoxide, forming carbon dioxide and desirable free hydrogen. Maintenance of suitable reaction temperature may require the addition of heat, which may be accomplished by the burning of an air and gas mixture over the catalyst bed. This operation introduces nitrogen. The gases leave the converter and return through the heat interchangers giving up their heat to the incoming gases. There may be an auxiliary converter operating at a point of suitable temperature in the interchanger system. There may also be special interchangers to save steam, or the steam may be condensed and discharged.

Addition of steam before conversion: The conversion of carbon monoxide by use of steam is essentially a continuation of the reaction in the water-gas machine, under more favorable conditions of temperature and steam concentration, as shown by the following reactions:

Gas generation .... $C + H_2O = CO + H_2$ (1)
CO conversion .... $CO + H_2O = CO_2 + H_2$ (2)
Total reaction (1)+(2) .... $C + 2H_2O = CO_2 + 2H_2$ (3)

In the first reaction, in the absence of a catalyst, high temperatures prevail, and 100 per cent excess steam is good practice. In the converter, with the aid of a catalyst, a lower temperature is used with many times greater excess of steam.

Steam may be introduced through steam interchangers, wherein the cooling of the exit gas is done by direct contact with a countercurrent spray of cold water in a long, circular condenser filled with suitable packing. The water emerges from the bottom of the condenser at nearly boiling temperature, and is fed to the top of the vaporizer, similar in construction to the condenser, where cold inlet gas is heated and supplied with steam from the hot water. The water is cooled by this treatment and again repeats its cycle through the condenser. In such an interchanger system about 4 volumes of steam per volume of inlet gas are used. Less than 10 per cent of this steam actually reacts, 60 to 70 per cent of it is interchanged, while the remainder is lost as condensate. The lost steam may be replaced by the addition of low-pressure steam to the inlet gas injected at a point just before the mixture enters the converters.

All the steam, 4 volumes per volume of inlet gas, may be injected as low-pressure steam into the inlet gas to the converter at a point in the heat interchanger system, and all the excess steam condensed and discharged. This method of operation requires almost three times as much steam and cooling water as does the method which utilizes the special steam interchanger. Condensation of excess steam may be accomplished in surface condensers, which must necessarily be large on account of the low heat transfer coefficient of the mixture of gas and steam to be condensed.

Heat interchange and catalysis: The mixed ingoing gases, with steam added, may be forced through heat interchangers, absorbing heat from the hot gases leaving the converter. The heat interchangers may be made of boiler-plate shells with internal nests of tubes. The inlet gases should flow around the tubes, and the exit gases through the tubes, so that external radiation losses are minimized and temperature transfer head improved. The shells should, of course, be heavily lagged to prevent heat loss. The interchangers should be carefully designed, so that the gases may enter the converter at as nearly the proper operating temperature as possible.

There may be one or two converters to each unit or set. The converters may be circular or rectangular shells of large cross-sectional area and with trays, supporting beds of catalyst in shallow layers through which the gas should pass freely and preferably in a downward direction to prevent disintegration of catalyst. The catalyst may be placed in a single layer, but great care is necessary so that the depth is not too great and so that the catalyst does not pack tightly and set up a large friction head. The catalysts were mainly of ferric oxide with the addition of some promoter[21] as chronium, cerium, or thorium. Such catalysts are chemically rugged against poisons, but are physically delicate and should be supported so as to avoid crumbling and packing. The catalyst temperature on the inlet side during operation of the converter will be about 500° C. with a rise in temperature across the catalyst of 50° to 60° C., due to the exothermicity of the reaction. This reaction heat should with very good heat interchangers be sufficient to maintain the system at its proper operating temperature, offsetting radiation and heat losses. In case additional heat is necessary for temperature maintenance, air combined with gas may be burned as a flame above the catalyst or in the bed itself. Flame combustion by means of a burner above the catalyst is a better method for heat development than burning air in the catalyst bed,[18] since the latter makes too large a temperature gradient through the catalyst itself. The procedure of course adds nitrogen to the system, and the more added here the less need be added in the gas manufacture.

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[21] B. A. S. F., Brit. patent 27,955 (1912); D. R. P. 292,615 (1912; D. R. P. 293,943 (1913); Fr. patent 469,907 (1913); Brit. patent 16,494.

Two converters in series may be used, the second at a lower temperature than that of the first. The use of such a secondary converter represents a decided improvement in operation, since the water-gas reaction has a much more favorable equilibrium at the lower temperature. It has, however, a much slower reaction rate. Thus it is desirable to accomplish most of the reaction at the higher temperature of the first converter and follow by the catalysis at lower temperature in the secondary converter. If air or oxygen be available during low-temperature catalysis, the oxidation of the carbon monoxide will be much more readily carried to its equilibrium value.

If equilibrium were attained during catalysis, a gas would be secured containing but 1 to 2 per cent CO. In practice this is not reached, and 2 to 4 per cent CO remains, representing a conversion of about 95 per cent of the original carbon monoxide. Due to the conversion, there is an increase of about one-third in the volume of the dry gases. The dry converted gas should have the composition shown in Table IV. This analysis may also be obtained entirely by calculation.

TABLE IV.—*Gas composition (dry) after conversion.*

	Per cent.
CO_2	29–27
CO	2–4
H_2	52–52
N_2	17–17
Total	100–100
X (CH_4, argon, etc.)	0.4–0.8

It will be noted that oxidation does not completely remove the carbon monoxide. It is necessary in a later purification process to remove the remaining 2 to 4 per cent.

The nitrogen content may be kept somewhat lower than is shown in Table IV in a case where it is desired to bring the gas ratio into proper proportion by addition of nitrogen in a later stage of the process.

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[18] Loc. cit., p. 99.

Deoxidation of electrolytic gas: Hydrogen made electrolytically and nitrogen made by the liquid-air process for synthesis to ammonia both contain small amounts of oxygen as an impurity. This oxygen must be removed before the gases are suitable for synthesis. The hydrogen and nitrogen gases are therefore taken from the storage holders and passed at low pressure through heat interchangers into a deoxidizer, which is a container filled with a suitable catalyst which may be copper shavings. Air may be burned in the deoxidizer to obtain the proper deoxidizing temperature, and also to introduce into the system any part, or all, of the required nitrogen. All oxygen originally in the hydrogen and nitrogen gases or that remaining from the burned air is consumed by the reaction in the copper. The hot deoxidized gas returns through the heat interchanger, giving up heat to the incoming gas. Control of the deoxidizer depends on the amount of nitrogen to be introduced into the system as air. Such an amount of nitrogen may be introduced here as is necessary to balance the hydrogen-nitrogen ratio, or if conditions are suitable, the complete nitrogen requirements of the process may be obtained by this method rather than from the liquid-air machines. It is, of course, necessary that care be taken not to introduce an excess amount of air, because all oxygen must be completely removed. Condensers are needed to remove moisture resulting from the combustion and to cool the gas before it enters the compressors. Such coolers may be built on the principle of surface or of jet condensers.

c. Purification of gas.—Compression of gas and removal of carbon dioxide: So far in the process we have been concerned with different methods for manufacture of gases and the oxidation of carbon monoxide in the water gases. These operations have taken place at low pressure, approximately atmospheric. The gases must now be compressed to high pressures for synthesis, and in the Bosch system must be compressed for purification purposes also. The purification pressures may, however, be less than the synthesis pressures.

The chief undesirable constituent in the gas at this stage in the Bosch process is carbon dioxide, which is removed by scrubbing the gas mixture with water at high pressure.[17, 19, 22] The dry gas drawn from the holders is compressed in a multistage compressor up to the pressure at which it is to remain through the rest of the process, or perhaps to some intermediate purification pressure. Scrubbing may be accomplished at pressures of 10 to 100 atmospheres, while synthesis may be at 100 atmospheres or more. Synthesis at 200 atmospheres would require five-stage compressors, which, for instance, with 25-

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[17, 19] Loc. cit., p. 99.

[22] Lane, Brit. patent 11,878 (1910); General Chemical Co. (de Jahn), Brit. patent 124,761 (1918); Greenwood, "Industrial Gases."

atmosphere purification, should be supplemented by three-stage machines to assist in handling the larger volume of gases in the lower stages before scrubbing. It will be noted that the carbon dioxide removed by scrubbing amounts to about one-third the total gas volume. The gases would be compressed in the first three stages of the five-stage machines, assisted by the three-stage machines, scrubbed, and then returned to the final stages of the five-stage machines for compression to synthesis pressure. Synthesis may be accomplished at 100 atmospheres pressures, in which water scrubbing may be accomplished at the same pressure, or at a lower pressure, as described above. One hundred atmosphere compression would require four-stage machines. There is no particular difficulty involved in construction of satisfactory compressors for pressures of 100 to 200 atmospheres, but a gas compressor of commercial capacity has not yet been developed to operate at pressures approximating 1,000 atmospheres. Care must be taken to prevent explosions due to possible suction of air into the compressors, and the compressor valves should be made of special alloy to withstand the corrosive effect of the gases. Compressor suction should be from a small holder floating on the line to take up variations of load.

The compressed gases are scrubbed in a long tower by passing upward countercurrent to water flowing downward over suitable packing. The packing should cause turbulent gas flow to permit the most intimate contact between water and gas, should not pack to cause channeling of gas or water, and should be resistant to pressure and corrosive action. The base of the scrubber should be constructed so that the water level will not rise into the towers. An electrical mechanism is more suitable for control of water level than is a float mechanism, because the force available from a float is not sufficient to transmit appreciable motion through a stuffing-box packing tight enough to withstand the high pressure within the scrubber. Sight gauges and manual control may be resorted to in emergency. There should be no restriction to the flow of gas into the tower or of water from the tower. Reciprocating pumps, in stages depending on scrubbing pressure, are satisfactory, but special material should be used in the valves to withstand wearing and pitting. The pumps may operate at constant speed, the control of water level being accomplished at the discharge from the scrubbers, or the speed of the pumps may be controlled by a water-level control mechanism. The former method is the more satisfactory, due to conditions of flow in the scrubbers. The composition of the gas after water scrubbing will be shown in the table following.

TABLE V.—*Gas composition after water scrubbing.*

	Per cent.
CO	3- 5
H_2	73- 72
N_2	24- 23
Total	100-100
CO_2	0. 1-1. 0
X(CH_4, argon, etc.)	. 5-1. 0

The solubility of carbon dioxide increases with its partial pressure. Table VI gives cubic feet of carbon dioxide at 60° F. and 30 inches Hg dissolved in 1 cubic foot of water. For a given CO_2 percentage in a gas, the scrubbing water necessary decreases with an increase of the total gas pressure. However, the energy required for pumping this decreased amount of water at the increased pressure is not greatly altered. At a given total gas pressure, the quantity of solvent water necessary is not greatly affected by variations in CO_2 concentration; since, as the CO_2 to be dissolved decreases, the solubility also decreases.

TABLE VI.—*Solubility of carbon dioxide in water.*[1]

CO_2 partial pressure.	0° C.	12° C.
Atmospheres.	*Volumes.*	*Volumes.*
5	9. 2	6. 5
10	17. 1	10. 3
15	23. 6	14. 5
20	28. 6	18. 2
25	32. 5	21. 6
30	36. 0	24. 8

[1] Société l' Air liquide, Brit. Patent 15,053 (1914).

Hence, CO_2 absorption should be completed in one stage rather than in a series of stages at decreasing concentration; that is to say, one long cylinder of proper cross-sectional area provides better scrubbing conditions than several shorter cylinders with the gas passing through them either in series or in parallel. High-pressure scrubbing decreases the size of apparatus required, since the volumes of gas and water are decreased proportionally while the velocity of absorption is increased, but the advantage of smaller apparatus is somewhat offset by the necessary increased strength of the vessel and the joints in pipe connections, etc. The above considerations generally point to comparatively low scrubbing pressure, that is about 200 to 500 pounds per square inch.

The scrubbing water with its dissolved carbon dioxide (and hydrogen sulphide), as well as some hydrogen and nitrogen, passes from the bottom of the scrubbing tower and discharges through a water wheel.[17, 19] Here the dissolved gases are liberated and much of the power used in pumping the water may be regenerated. Specially designed apparatus is necessary for the recovery of power from a mixture of expanding gases, vapors, and water. Power can not be recovered efficiently by use of the common types of water wheel nozzles when gases are dissolved at high pressures in the operating liquid. The composition of the gas escaping from the dissolving water after pressure release will be normally as shown in Table VII, the variation depending upon operating conditions.

TABLE VII.—*Composition of dissolved gas released from scrubbing water.*

	Per cent.
CO_2	76– 84
H_2	17– 11
N_2	6– 4
X (H_2S, CO, etc.)	1– 1
Total	100–100

Operation shows that about 1 volume of hydrogen and nitrogen is dissolved with every 4 volumes of carbon dioxide in spite of the fact that this is about twice that called for by the available data on relative solubilities. This loss represents about 10 per cent of the total of these gasses manufactured. The total gas removed in the water scrubbers represents about 35 per cent of that manufactured. The loss of hydrogen and nitrogen is theoretically independent of the pressure at which the scrubbing is done and is unavoidable since the solubility of these gases is not negligible.

The carbon dioxide in the liberated gases is a valuable by-product. In conjunction with the ammonia synthesized, it may be used for the manufacture of ammonium sulphate by the decomposition of gypsum in the presence of ammonia, or it can be used in the ammonia soda process.[23] There are available from the Bosch process about 45,000 cubic feet of carbon dioxide per ton of ammonia synthesized.

The residual carbon dioxide (0.1 to 1.0 per cent) remaining after water scrubbing may be removed by washing the gas with a cold caustic solution.[24] This may be done simply by bubbling the gas through a tower filled with solution. The caustic may be replenished periodically, since large quantities are not required.

Removal of carbon monoxide: The next impurity to be eliminated after removal of carbon dioxide in the water scrubbers is

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[17, 19] Loc. cit., p. 99.

[23] C. Bosch, Z. Electrochem., 24 (1918), 361.

[24] Wroblewski, Compt. Rend., 94 (1882), 1,355; Bohr and Bock. Wied, Ann. Phys. (2), 44 (1891), 318.

the remaining 3 to 5 per cent of carbon monoxide. This is done by scrubbing the gas with an ammoniacal cuprous solution. If an intermediate pressure has been used for water scrubbing, the gases are returned to the high-pressure compressors to complete the compression and then passed upward through a scrubber similar to the water scrubber. A cuprous solution[20] is employed as the dissolving medium, the solution passing downward through the scrubber, countercurrent to the gas. The spent cuprous solution coming from the reservoir at the bottom of the scrubber passes on through pressure release vessels to a regenerating system where its carbon monoxide is removed by heat.

No attempt is made to recover power from the copper solution as it leaves the scrubbers, since the energy requirement for pumping the solution is small. Regeneration may be done in vats under vacuum, where the solution is heated by steam coils to a sufficient temperature to expel the gas from the solution. Continuous regenerators may also be constructed, using a tubular construction for heat transfer purposes, accomplishing the expulsion more economically than is done by steam-heated vats. The composition of the solution may require readjustment before it is again used.

Scrubbing the gas with the ammoniacal cuprous solution removes by reaction with the reduced copper any oxygen that may be present; removes by combination with the free ammonia the carbon dioxide residual after the water scrubbing, as well as traces of other acidic gases that may have passed through the water scrubbers; and absorbs nearly all of the 3 to 5 per cent of carbon monoxide in the gas. There is also dissolved about 1 per cent of the nitrogen and hydrogen which is liberated with the carbon monoxide during regeneration of the cuprous solution. The by-product—carbon monoxide—may be recovered for use in other processes or it may be injected into the conversion system to combine with steam to produce hydrogen.

Refrigeration is of valuable assistance in the purification of the gas with cuprous solutions. The gas before entering the scrubber may be passed through coils cooled with brine, and the copper solution on the way to the scrubber may be similarly cooled. Cooling does not greatly increase the absorption capacity of the solution at saturation, but it does decidedly decrease the carbon monoxide vapor pressure of the solution when it is but partially saturated. Thus refrigeration does not materially decrease the amount of solution to be used, but it does improve the purity of the gas at the exit of the copper towers where it is in contact with fresh solution. Table VIII gives the impurities in the gas leaving the copper system.

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[20] Loc. cit., p. 99.

TABLE VIII.—*Impurities in gas after cuprous scrubbing.*

	Per cent.
CO_2	0
O_2	0
CO	0.1–0.01
NH_3	0.2–0.01
H_2O	0.02—less.
X (CH_4, argon, etc.)	1.0–0.5

As in the water scrubbers, better scrubbing is obtained when the flow of the gas through solution occurs in a long tower with properly restricted cross-sectional area rather than through several shorter towers, with the flow either in series or in parallel. The towers should be equipped with suitable reservoir, level-control devices, and auxiliary equipment such as pumps, pressure-release vessels, etc.

Both cuprous carbonate and formate solutions have been commercially used for the absorption of carbon monoxide from gases. There seems to be very little difference in absorptive power between the two, but there is considerable advantage in using the formate when stability of the solution is taken into consideration. A carbonate will precipitate metallic copper while in use and will break down during its regeneration.

The completeness of purification of the gases by copper solution is greatly improved by pressure. It is, therefore, advantageous to operate the copper scrubbers at more than 25 atmospheres pressure, usually at the pressure at which synthesis is done. The increased pressure also permits the construction of smaller apparatus. Efficiency of purification by the copper solution is of considerable importance and minimum quantities of solution should be used on account of the cost of manufacture and regeneration.

Attempts have been made commercially to remove most of the carbon monoxide by a concentrated hot caustic solution[19, 25] preliminary to the cuprous scrubbing. Carbon monoxide and hot caustic soda produce sodium formate directly. Chemically the carbon monoxide removal was satisfactory, reducing the 3 to 5 per cent inlet carbon monoxide down to under 1 per cent when the optimum caustic concentration of 10 per cent[26] was used at temperatures around 200° C. However, the residual carbon dioxide in the gas causes a precipitation of insoluble carbonate from the solution. The mechanical difficulties attending the use of hot caustic are also very great because of its corrosive action and the elaborate equipment required. The consumption of hot caustic under operating condi-

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[19] Loc. cit., p. 99.

[25] B. A. S. F., Brit. patent 1,759 (1912); U. S. patents 1,126,371 (1915); 1,333,087 (1915); D. R. P. 254,043 (1911); D. R. P. 279,954 (1913).

[26] F. A. Weber, "The Action of Carbon Monoxide on Caustic Soda," Dissertation, Karlsruhe, 1908; G. R. Fonda, "The Action of Carbon Monoxide on Alkalies," Dissertation, Karlsruhe, 1910.

tions is prohibitive unless improved methods of recovery are developed.

Additional purification: After the cuprous scrubbing further purification may be necessary, depending on the sensitiveness of the catalyst used for the ammonia synthesis. Where comparatively rugged catalysts are used, as in Germany, there are no steps taken to remove moisture or minute quantities of carbon monoxide which are retained after scrubbing. Where sensitive catalysts are used it is necessary that purification be carried to the furthest degree. This is true whether the gases be manufactured by the Bosch process or by electrolytic and liquid-air processes. In either case refrigeration should be utilized to remove most of the moisture, and some material, such as soda lime or sodamide,[19] following the cooler, should be used to desiccate the gases.

Electrolytic hydrogen and liquid-air nitrogen for synthesis to ammonia do not, of course, require the great amount of purification that the water gas requires. After deoxidation the mixture of electrolytic gas and nitrogen is ready for compression and then introduction into the synthesis system through a suitable drier and filter to eliminate any remaining moisture or foreign substances which may have entered into the gas during compression.

d. Synthesis of ammonia.—Heat interchange and catalysis: The purified gas, consisting of about 3 parts hydrogen to 1 part nitrogen with 0.5 to 1 per cent of inert gases, such as argon and methane, passes into the ammonia synthesis system. The synthesis of ammonia in processes which operate at 100 to 200 atmospheres can be accomplished in one portion of a continuous circulating system by passing the nitrogen-hydrogen mixture through circulating compressors into heat interchangers and into the converter containing a suitable catalyst. The gases containing the synthesized ammonia return through the heat interchangers into another portion of the circulating system, where the ammonia is removed continuously by liquefaction or absorption, while the uncombined gas, together with additional gas mixture introduced to replace that synthesized, repeats the cycle. The circulating system may also contain heaters at the inlet of the converter for maintenance of system temperature as well as gas meters, filters, temperature measuring devices, etc.

Synthesis in processes operating at 600 to 1,000 atmospheres pressure and high temperature has been accomplished in a series of converters, residual gas passing from the first to the second, etc., with final rejection of any remaining uncombined gases. This method is, however, not desirable on account of the inefficient use of converter and on account of the loss of gas at the exit. The use of duplicate converters in this series means that each succeeding converter operates on a lesser volume of gas. This might, of course, be overcome by the use of varying sizes of converters, but such a procedure would be very impracticable on account of the desirability for duplication of parts. In a combined circulating and series system in which only two converters would be used and with the large ammonia concentration obtained at these pressures, it would only be necessary to recirculate about one-third of the gas volume. Ammonia would be removed at the exit of each converter and the remaining one-third of the gas reduced in pressure and injected into one of the intermediate stages of the compressors, where it would mix with fresh incoming gas and be recirculated. Operation at pressures as used by Claude offers the advantage of smaller apparatus, although it must be of heavier construction than is necessary for operation at the lower pressures.

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[19] Loc. cit., p. 99.

A process operating at 300 atmospheres or more should obtain an ammonia yield of 15 to 18 per cent. A circulating system, a converter series, or a combination of both, might be adopted, but it is likely that a circulating system is the more practicable.

The reaction for ammonia synthesis is:

$$N_2+3H_2=2NH_3.$$

The extent to which this reaction progresses depends upon the equilibrium of the system, which is a function of the temperature, pressure, and relative concentration of the constituents. As in carbon monoxide conversion, the equilibrium is more favorable at lower temperatures, although the reaction velocity is greatly decreased, and the catalysts become more sensitive to the action of impurities in the gases. The equilibrium is also favorably effected and the reaction velocity increased by a rise in pressure. The effect of comparatively large variation from the ratio of 3 hydrogen to 1 nitrogen is small, although the maximum ammonia concentrations and greatest reaction velocities are obtained with the theoretical mixture. Table IX shows the effect of pressure on the equilibrium of ammonia concentrations for the reaction in a 3:1 mixture.[27] The percentages shown for 500 atmospheres have been obtained by extrapolation and are not absolutely accurate. They indicate the values closely enough for purposes of comparison.

TABLE IX.—*Equilibrium, NH_3, per cent.*

Temperature.	30 atmospheres.	100 atmospheres.	200 atmospheres.	500 atmospheres.
° *C.*	*Per cent NH_3.*	*Per cent NH_3.*	*Per cent NH_3.*	*Per cent NH_3.*
400	10.7	25.1	36.3	52
500	3.6	10.4	17.6	31
600	1.4	4.5	8.2	17
700	0.7	2.1	4.1	9

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[27] Loc. cit., 14, p. 96.

Reaction velocities are increased in the presence of a catalyst, so that a lower temperature with a more favorable equilibrium may be used. In practice the speed of the gas through the caltalyst is chosen so that the equilibrium concentration of ammonia is not reached. The activity of the catalyst and the rate of flow will control the actual ammonia yield. The catalysts for this reaction as a class are very delicate chemically,[28] and small amounts of carbon dioxide, oxygen, or moisture greatly decrease their activity, while carbon monoxide is also quite harmful. A catalyst which may be an excellent reaction promoter for pure gases will become a poor one in the presence of very small quantities of these impurities. It may, for instance, on test indicate a 15 per cent conversion on pure gas at 100 atmospheres, but it can not be recommended for general use, since the different impurities in various commercial gas compositions will greatly impair its activity. The particular catalyst must be chosen for the particular gas composition with which it will come in contact. The catalysts are mainly of reduced iron with various promotors added [17, 19, 29]. The question of proper speed of the gas over the catalyst, that is to say, the space velocity at which a catalyst may be operated is of considerable importance. As the space velocity is increased, the percentage of ammonia in the exit gas is decreased, though not in as great proportion. Thus a greater total yield in weight of ammonia is obtained by an increase in space velocity.

A large concentration of ammonia gives a large temperature rise over the catalyst due to the exothermic reaction. This is the important factor in the operation of heat interchangers and in the maintenance of temperature of the entire system. The percentage of ammonia given by the catalyst also controls the number of times a given quantity of gas must be recirculated before complete synthesis is obtained or, in the case of the French process, it governs the number of converters through which the gas must be passed for complete synthesis. Therefore it governs the size of all the apparatus in a circulating system where such is used, and in the French system it governs the number of pieces of equipment necessary.

With the present development of ammonia synthesis, temperatures of the order of 450° to 600° C. are employed. The reaction is exothermic to an extent sufficient to cause more than a 15° C. temperature rise of the gases for each per cent of ammonia produced. The temperature gradient thus developed across the catalyst is available for maintaining heat interchange between exit and inlet gases through suitable interchanger apparatus. The heat evolved in the higher pressure systems, where large conversions are obtained, is in

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[17, 19] Loc. cit., p. 99.

[28] Greenwood, loc. cit., patents by de Jahn, Haber and Le Rossignol, Bosch and Nittasch.

[29] General Chemical Co. (de Jahn), U. S. patents 1,141,947 (1915), 1,143,366 (1915).

excess of that required and, therefore, presents the problem of cooling rather than of heating, but also makes possible automatic reactions with small installations which are the more adaptable to manufacture of ammonia from small quantities of hydrogen obtained as a by-product in the chemical industry. With proper design sufficient heat interchange surface and high conversion in the lower pressure systems, the heat evolved in the reaction may offset all the heat losses. The supply of additional heat to the system is an important and serious problem.[30] Heat may be added either for temperature maintenance during operation, or for starting either by internal combustion within the catalyst bomb or by the use of a heater which may be internal or external to the bomb. A combustion device may use oxygen (or pure air) and hydrogen (or reaction mixture) under pressure. The burner for combustion may project through the top of a converter maintaining the flame in the direct path of the gases just before they enter the catalyst bed. This method of supplying heat forms moisture and passes it on through with the reaction gases to the catalyst. Heat may be added to the system by the use of externally fired heaters placed at the inlet of the converter. Safety and efficiency is difficult to obtain in this type of heater on account of the temperature and pressure of operation. The most practicable method for addition of heat is by means of an electrical heater, preferably within the converter, by which the gases may be brought to any desired temperature. Such a device has the advantage of increased safety over externally fired heaters, operates at much greater efficiency, allows no loss of pure hydrogen, presents no difficulties due to moisture in the gases, and provides better temperature regulation.

The ammonia equilibrium at operating pressures of 600 to 1,000 atmospheres is so high that more heat than is necessary for temperature maintenance is given off by the reaction. This heat must be extracted without affecting the strength of the apparatus or the effectiveness of the catalytic or reaction conditions. It presents a difficult problem, but one which Claude believes he has solved. An excess of heat at these pressures is in contrast with an insufficiency at lower pressures. The pressure at which an equilibrium between the heat given off and that generated may be obtained to keep the system at desired temperature is not strictly definable, since it depends entirely on the design of apparatus, control of operation, and on the quality of catalyst used. Temperature may be maintained at 100 atmospheres and with conversions as low as 5 per cent, but the actual accomplishment requires complicated design and most thorough insulation of apparatus. With an increase in conversion due to increase in pressure or to better quality of catalyst, the problem of design becomes somewhat easier, although care must still be taken in maintaining proper temperature gradient throughout catalyst, unless one desires to accept an inefficient use in volume of catalyst required.

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[30] B. A. S. F., D. R. P. 259,870 (1911), 268,929 (1912).

The effect of moisture on the catalyst is a point to be considered very seriously. Combustion resulting in production of 1 per cent of moisture will cause a rise in temperature of about 70° C. at the catalyst, but the activity of the catalyst will be materially decreased. In plants where water scrubbing or absorption is used to remove ammonia from the gases after synthesis, all the circulating gases carry some moisture. A type of catalyst must be used that can remain in action in the presence of moisture, but activity of a catalyst as a reaction promoter in such an atmosphere is greatly decreased and its optimum operating temperature is increased. Certain catalysts are rendered entirely unusable with moisture, while without it they are highly active and desirable catalysts. The ammonia equilibrium for 200 atmospheres pressure and 500° C. calls for 17.6 per cent ammonia, but would probably make available 10 per cent ammonia with catalyst operating on pure gas. Actual operation with moisture would make available less than one-half this amount, and, further, the reduced reaction would decrease the generation within the bomb and the temperature head across the heat interchangers, making it increasingly more difficult to maintain temperature. It therefore becomes a question as to whether to use the more troublesome method of refrigeration for ammonia removal, and by so doing benefit by the use of much more active catalysts in the dry gases, or whether to utilize the easier method (water absorption) and use less active catalysts in moisture-laden gases.

Removal of ammonia and circulation of gas: There are two methods just mentioned for removal of ammonia,[19, 31] one, by liquefaction and mechanical separation, the other by absorption of ammonia in water. Liquefaction delivers the product in the anhydrous form, while absorption delivers it as a solution, from which it may be desirable later to free the ammonia by distillation. Removal by liquefaction causes no catalyst troubles due to moisture left in the gases. It, however, consumes more power than does removal by absorption.

The ease with which liquefaction by cooling is carried on is determined by the ammonia concentrations and the synthesis pressures utilized. For instance, about —40° to —50° C. may be required to liquefy ammonia completely enough when pressures of 100 atmospheres are used; about —10° to —20° is required for the same effi-

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[19] Loc. cit., p. 99.

[31] B. A. S. F., D. R. P. 235,521 (1908); D. R. P. 259,996 (1911); D. R. P. 270,192 (1912); U. S. patent 1,202,995 (1916).

ciency of removal at pressures of 200 atmospheres, while liquefaction can be attained completely enough with water cooling when 600 to 1,000 atmospheres are used. Very low temperatures are essential in the lower pressure processes, especially when low conversion is obtained. Thus, if 4 per cent ammonia were delivered by the catalyst at 100 atmospheres pressure, with only —10° C. in the liquefier, nearly half of the ammonia would return to the catalyst inlet. For the low temperatures necessary in operation at 100 to 200 atmospheres pressure, special designs and construction of refrigeration equipment are necessary. When employing liquefaction with a circulating system, at 100 to 200 atmospheres pressure, the gas containing the ammonia passes from the converter through the heat interchangers and into the liquefaction coils which are externally and separately cooled by a refrigerating system. The ammonia gas is liquefied and may then be removed by mechanical separators or traps at the exit of the liquefiers, while the gas, still containing some residual ammonia, passes back through interchangers and to the circulating pumps to repeat its cycle. The amount of residual ammonia in the gas will depend upon the temperature reached in the liquefier as is indicated in Table X.[32] Operating factors, of course, prevent achievement of liquefaction to the theoretical limit.

TABLE X.—*Vapor pressure of liquid NH_3.*

Temperature.	NH_3 vapor pressure.	NH_3 at 200 atmospheres.
°C.	*Atmospheres.*	*Per cent.*
0	4.2	2.1
—10	2.8	1.4
—20	1.83	0.91
—30	1.16	0.58
—40	0.68	0.34

To maintain temperatures of —40° C. or less as required for operation of a 100-atmosphere plant it is necessary to expand the refrigerating ammonia to a considerable vacuum, and it is required that the compressors operate at that vacuum on the suction stroke. Thus, if ammonia is used as the refrigerant, two-stage compression will be necessary. Standard machines operating with ammonia may, however, be used, operating with compound compression of refrigerant for one low-temperature or second-stage liquefier, while another or first-stage liquefier may be operated within a nearly normal ice-making cycle. Carbon dioxide could be used as a refrigerant material in ammonia synthesis systems, but its use would present no advantages over the more commonly used ammonia refrigerant, and it would have the disadvantage of operation at higher pressures.

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[32] G. A. Goodenough: Properties of Steam and Ammonia (J. Wiley & Sons (Inc.) (1915).

Carbon dioxide compressors would also be somewhat more complicated than the ammonia machines.

The removal of condensed ammonia from high-pressure gas is difficult, since the condensate is partially in the form of a fine mist which is difficult to precipitate or agglomerate. In the separation of water from steam, we are involved with specific gravity ratios of 150 to 1 while, in the case of ammonia and high-pressure gas, the ratio is 15 to 1. Thus, ordinary steam separators are not suitable. High velocities, low friction of the gas stream over the separating surfaces, and immediate removal of the separated liquid from contact with the gas are essentials of a good separator.

If absorption of the ammonia be the method of removal, the gas mixture, still under pressure, is scrubbed with water. This is best done in several stages with efficient cooling throughout, since the heat of solution is very considerable. The absorption apparatus may consist of scrubber towers similar to the cuprous scrubbers, or it may consist of water-cooled coils through which the gas and absorbing water are forced in intimate mixture. The water may be discharged with an ammonia concentration corresponding to commercial aqua ammonia, or even higher if desired. The uncombined gases leave the absorbers and are recirculated to the heat interchangers and converter.

The high-pressure gas in passing through the absorber system gives up most of its ammonia to the water, only about one-fourth per cent remaining in the gas. This ammonia content will depend on the temperature at which the last gas stage of absorption was maintained and on the ammonia concentration of the aqua emerging from this last stage together with the gas. Evidently the more water used for absorption the less is the residual ammonia in the gas. However, the hydrogen and nitrogen dissolved and the power required will increase with the increase of water, and this represents some small loss in the efficiency of the system.

Circulating system in general: The circulating pumps are located between the liquefaction system and the converter, with "make-up" either preceding or following the pumps. In the first case the pumps directly handle the "make-up" gas together with the circulating gas, but the total pressure of the system is higher by the amount of the differential pressure of the circulating system, since the "make-up" pressure is determined by the pressure of the purification system.

The volumetric efficiency of circulating pumps is much reduced when they are operated without lubrication because of the large piston clearance necessary in such case. It is better to put rings on the pistons and where possible lubricate, and then, by filtration, remove oil in suspension from the gases before they pass on to the catalyst.

The speed of circulation of the gases affects the operation of catalysts as before mentioned. Operating conditions, such as the use of new catalysts, better equipment, etc., permitting greater production, may make it desirable to increase the speed of circulation. Such increase may be limited by any of the following: (1) Insufficient heat transfer to maintain the temperature of the ammonia converter sets, (2) insufficient capacity of the purification system to supply the necessary gas for the increased yield, (3) insufficient capacity of the ammonia removal installation to take care of the increased yield, (4) excessive friction to gas flow in the apparatus of the circulating system.

The supply of hydrogen and nitrogen to the synthesis system should be in the average ratio of 3 to 1 to avoid the accumulation of an excess of either constituent. The chemical composition of the supply can be best controlled by analysis of the gases in the circulating system where the cumulative effect of any slight inaccuracy of adjustment can be detected. The adjustment, if small, may be made by the injection of pure nitrogen or hydrogen obtained by liquefaction.[83] It is well to run toward high hydrogen in the supply so that the adjustment may be entirely with nitrogen. Nitrogen may have a use other than for balancing the gas ratio. With a suitable shell construction, the nitrogen may be used to flush the inner walls of the ammonia converter, which otherwise are subjected to the deleterious action of hydrogen and ammonia. As previously stated, it is very difficult to maintain the proper gas ratio by regulation at the producers. The use of pure nitrogen for regulation is a much more satisfactory method of operation.

The inert gases, methane and argon, are present to the extent of 0.5 to 1 per cent in the "make-up" entering the circulating system, and tend to accumulate as the hydrogen and nitrogen are being removed in the form of ammonia. Some method of removal of this accumulation must be employed. The simplest method for continuous operation is to allow a fraction of the circulating gases to continually escape. Purging a quantity of gas from the circulating system equivalent to 10 per cent of the entering "make-up" gas will maintain a concentration of inert gases of 5 to 10 per cent. The effect of inert gases on the catalysts of ammonia is very decided, due to the lowering of the equilibrium, but, on the other hand, the loss of purified hydrogen and nitrogen in the purge is costly, although the hydrogen may be burned under boilers. In operation the choice as to the proper purge is generally fixed by the unavoidable leakage in the system. Thus the leakage may never be below 10 per cent of the "make-up" gas, and therefore the concentration of the inert would never be above 5 to 10 per cent, and no additional purge would then be necessary.

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[83] B. A. S. F., D. R. P. 265,295 (1912), 1,075,085 (1913).

Construction of heat interchangers and converters is an important problem. The sizes of the shells is a function of the capacity and operating pressure of the system. They have been made as large as 48 inches inside diameter and 40 feet long, the longer shells having been joined in the middle. They are made of hollow forged alloy steel, some with special forged alloy liners. The grain structure in castings is not sufficiently close to permit their use against nitrogen and hydrogen gases, and pressures of 100 atmospheres or more. Special attention must be given to the design of the joints at the heads of the shells so that they will remain tight against the tremendous internal pressures and against vertical and lateral strain caused by differential temperatures in head, shells, and bolts. Hydrogen at high temperatures and pressures readily diffuses through steel and within the steel combines with carbon to form methane, which is not diffusible, thus causing blisters and other dangerous imperfections. Ammonia, at temperatures of formation or decomposition, has a powerful action on iron tending to completely break down its crystalline structure, probably by nitrification. Furthermore, the tensile strength, proportional limit, and other structural properties of steels rapidly and dangerously decreases with increase of temperatures above 300° C. Operation and various tests indicate that chromium vanadium and tungsten alloys, forged, best withstand the severe conditions.[19, 34, 35]

Some unique methods have been devised for the internal construction of converters whereby the most efficient operating conditions are provided for the catalytic reaction. Proper temperature maintenance and temperature distribution for the reactions is one of the chief difficulties. For the low-pressure systems the heat evolution is often insufficient, while excess heat is one of the chief difficulties with the superpressure systems. For the latter, the French claim to have a design of converter which is able to remove the excess heat and at the same time not interfere with the strength of the bomb or the reaction conditions for the catalyst.

If the ordinary tube nest construction of heat interchanger be used, it should be made of small single tube of great length of path and with total cross-sectional area sufficiently small to allow considerable velocity of the gases without at the same time producing excessive friction. Nest constructions where one or two tubes are placed con-

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[19] Loc. cit., p. 99.

[34] Loc. cit., p. 121.

[35] B. A. S. F., D. R. P. 254,571 (1911); D. R. P. 256,296 (1911); D. R. P. 275,156 (1911); U. S. patent 1,188,530 (1916).

centrically within another are not advisable on account of their very complicated and difficult construction, difficulty in repair, and on account of the friction head set up when the constructions are faulty. Special inlet and outlet connections from the nest and passing through the heads are essential to allow for expansions and contractions due to temperature differences.

Particular care in design must be taken throughout the entire system to allow for expansions and contractions due to changes in operating temperatures. On this account and because of the high gas pressure and temperature, special pipe fittings, valves, etc., and provisions to take up expansions and contractions are required. The number of fittings should be reduced to the smallest convenient number, and turns in piping should be effected by use of bends rather than by use of ells, tees, etc., to keep system friction at a minimum, and to avoid possibilities of leaks, especially in the hot portion of the circulating system.

Great economy may be effected by proper use of heat-insulating materials. A range of temperatures from 600° C. to –50° C. is found in this process. In most cases it is advisable to wrap the equipment with material, but, where the apparatus must be accessible at all times, it may be advisable to build removable forms of insulating material, or in other cases to build heat-tight rooms, as, for instance, parts of the liquefying apparatus may be set up in rooms made of cork.

Ammonia disposal: The ammonia which has been removed from a system by cooling and liquefaction may be discharged into a high-pressure storage chamber, from which it may be piped to other parts of the plant for utilization, or it may be discharged into small cylinders for shipment. When the liquid ammonia is to be oxidized to make nitric acid, it may be expanded from the high-pressure system into a vaporizer, generating much refrigeration which may be utilized in the original liquefaction.

When the product is in the aqueous form it may be stored in large tanks and utilized as desired or it may be shipped in tank cars.

3. Leading Plants of the World.

a. German plants.—Two plants were built in Germany, one at Oppau with 110,000 short tons ammonia annual capacity, and one at Merseberg with 220,000 short tons capacity. These plants operated at 200 atmospheres pressure. Preliminary work was started on the Oppau plant in 1912, and by 1914 a pilot plant of about 10,000 tons annual capacity was in operation. The main plant construction was started in 1914, and capacity operation reached in 1917. The Merseberg plant was built mainly during the war, and three-quarters of its rated capacity was in operation before the armistice was signed. Both plants were designed and built by the Badische Aniline und

Soda Fabrik after several years of experimental and development work. The same company also operated the plants, although the Government aided them in many ways during the war.

Primary central power for the German plants is furnished by producer gas engines and steam turbine installations. In addition, there are steam and gas engines for local power production at various points throughout the plant. High-pressure steam is furnished by water-tube boilers using principally lignite as fuel, although some of the boilers are equipped for burning tar and oil and others for producer gas. Low-presure steam is furnished by tubular boilers which are heated by gas-engine exhausts. There was some coke purchased during the war, but this was later to have been furnished by a coke-oven installation in the process of construction. The buildings are of substantial mill-type construction. The plants were well equipped with auxiliary facilities, such as machine shops, pipe shops, etc.

b. American plants.—Two plants have been built in the United States, one by the United States Government at Sheffield, Ala., and one by the Atmospheric Nitrogen Corporation at Syracuse, N. Y. The plant at Sheffield was built as a war emergency measure in 1917. Its rated annual capacity was 11,000 short tons of anhydrous ammonia and its operation was at 100 atmospheres pressure. It followed generally the German Haber process, but its construction was based directly on experimentation, and designs developed by the General Chemical Co. over a preceding period of several years. Experimental operation of the gas and purification systems was started in June, 1918, and of the synthesis system in September, 1918, but continuous operation was not realized up to the time the plant closed in January, 1919. The plant consists of a water-gas plant, ammonia-process building, power house, and auxiliary facilities. Buildings are of substantial brick and steel construction. Electric power was furnished by a steam plant which consumed bituminous coal. High and low pressure steam were furnished from the same power house.

In 1920 the Atmospheric Nitrogen Corporation, formed by the General Chemical Co. and the Solvay Process Co., commenced construction of a synthetic ammonia plant at Syracuse, N. Y. The plant has a capacity of 10 tons of anhydrous ammonia per day, and is constructed in accordance with designs substantially similar to those for the ammonia process at United States Nitrate Plant No. 1, incorporating, however, such modification as trial operation at Sheffield indicated to be necessary.

The Syracuse plant consists of a steam-boiler plant, gas plant, conversion and process buildings, which are of substantial mill-type construction. The plant is laid out so as to be easily capable of expansion, and is adjacent to the Solvay Co.'s soda process, which may, if it later proves desirable, utilize the by-product, carbon dioxide, from the ammonia plant. The cost of construction of this plant was about $4,000,000. In the initial operation the plant operated at more than rated capacity, and the corporation is confident of continuous operation with only such interruptions as are necessary from time to time to eliminate minor troubles.

c. *English plants.*—The British Government in 1917 commenced work on the erection of a synthetic ammonia plant at Billingham, Durham, but only a small amount of preparatory work was completed when the armistice was signed and work on the plant was suspended. The Government has since turned over the continuation of the work to a private corporation, Messrs. Brunner, Mond & Co., which has taken over the Government's leading engineers and chemists, and is now building a plant at Billingham for the manufacture of about 10 tons of ammonia per day, with provision for extension. The process to be used is essentially a modification of the German Haber process, but has been worked out entirely without German assistance. There has been no other commercial construction of synthetic ammonia processes in England.

d. *French plants.*—There have been no commercial plants for the manufacture of synthetic ammonia in France. The French have, however, been quite active in the investigation of synthetic ammonia processes. M. Georges Claude conceived the idea of utilizing what he terms as "super" pressure for the combination of nitrogen and hydrogen to form ammonia, and has developed a semicommercial installation operating at 600 atmosphers pressure and has patents covering pressure up to 1,000 atmospheres.

e. *Italian plants.*—Casale has developed in Italy a process which operates at 300 atmospheres pressure. A catalyst was found after long experimentation at the conclusion of the war, which, it is claimed, continued to function despite impurities found in hydrogen and nitrogen gases. Accordingly, the Italians constructed at Terni a plant with a capacity of 1,200 tons of ammonia per year. This plant uses electrolytic hydrogen produced by the energy obtained from the great waterfalls at Terni. Hydrogen is burned with air to obtain nitrogen. The nitrogen-hydrogen mixture is heated and passed under high pressure into a cylinder containing the catalyst. The ammonia produced is condensed by means of refrigerating apparatus, and is discharged into steel cylinders.

4. Construction and Operating Costs.

a. *Costs in Germany.*—The entire construction cost chargeable to the plant at Oppau, Germany, will total, perhaps, 250,000,000 marks. If the original pilot plant, the coke plant, the ammonia utilization plants (i. e., ammonium sulphate, nitric acid, etc.), be neglected and corresponding reductions made in the general facilities investment, the cost chargeable to the manufacture of ammonia alone is estimated at about one-half the entire cost, or some 125,000,000 marks, which may be divided, about one-third for buildings and construction and two-thirds for equipment and machinery. The former includes buildings, foundations, roads, trackage, and all general construction; the latter covers special equipment or machinery and includes its installation cost. This is an estimate of actual prewar (1914) cost and would mean an investment of about $270 per annual short ton of ammonia capacity, or $100,000 per daily ton. This cost is applicable only to the conditions existing in Germany in 1914. The construction costs in 1916 at Merseberg showed an increase of more than 50 per cent over the Oppau figure, due to the rising labor and material charge. The 1917 estimate, based on the construction costs for the last one-fourth capacity of the Merseberg plant, showed an increase of 150 per cent over the 1914 figure (1914, $270; 1916, $400; 1918, $700). The estimate below gives the cost of ammonia per ton, as produced at Oppau in the form of aqua in 1914–15, at the time the plant was developed. The cost in German marks for 1918, based on Merseberg experience and prices then existing, may be taken at about two and one-half times the 1914 figure. Any figure which might be given for post-war conditions would be, to a large extent, meaningless in view of the unsettled conditions and the prevailing rates of exchange.

Plant production cost per ton of ammonia at Oppau, Germany, in 1914.

	Marks.	
Labor operating:		
35 enginers, at 10,000 marks per annum	3.2	
66 man hours per ton, at 0.6 marks per hour	39.6	
	42.8	($10.27)
Fuel:		
2 tons coke, at 20 marks	40.0	
1 ton coal, at 15 marks	15.0	
2 tons lignite, at 10 marks	20.0	
	75.0	($18.00)
Plant upkeep:		
Repair and maintenance, at 6 per cent	68.2	
Depreciation and amortization, at 6 per cent	68.2	
Development and obsolescence, at 4 per cent	45.5	
	181.9	($43.66)
General works expense:		
Unclassified expenses, 10 per cent of above	30.0	
Incidental materials, 5 per cent of above	15.0	
	45.0	($10.80)
Fixed charges:		
Interest, insurance, taxes, at 9 per cent	102.3	($24.55)
Total production cost per short ton	447.0	($107.28)
Total production cost per pound NH_3	0.2235	($0.364)

b. Costs in America.—The total cost chargeable to the manufacture of ammonia at United States Nitrate Plant No. 1 would have been approximately $8,000,000 to complete the plant in a most substantial manner to a capacity of 11,000 tons of ammonia per year. This figure represents an estimate of the cost under emergency conditions and may be reduced to almost half of that amount to represent pre-war costs. Thus the pre-war cost per annual ton of ammonia in this country would have been about $400, or possibly less, which compares quite favorably with the German costs. The same plant could probably be reproduced to-day at not more than $500 per annual ton.

Operation of this plant was of an intermittent nature and with production at no time approaching rated capacity, so that it was impossible to obtain proper costs for actual operation. The present-day investment cost per annual ton of ammonia for a 11,000-ton per year water-gas ammonia plant may be assumed, from the above, to be $500. A comparative investment cost of ammonia made from electrolytic hydrogen would be $400 per annual ton. There follows a summarized comparative estimate of the cost of ammonia per ton by both methods of manufacture based on the above investment costs, which will be distributed to buildings and machinery in the same proportion as was done in previous estimates carefully made by the plant 1 section of the Nitrate Division for plants of the above capacity and operating at 100 atmospheres pressure. An allowance of 12½ per cent on buildings, 15 per cent on electrolytic cells, and 20 per cent on other equipment may be made for depreciation, amortization, obsolescence, interest, taxes, insurance, etc., and 2 per cent on buildings and cells and 5 per cent on the equipment for repairs and maintenance. The individual percentages allowed here differ slightly from those in the estimate of German costs, but their aggregate of overhead charges is approximately the same for both estimates.

In the estimates referred to above, and from which much of the data for the following estimate has been taken, the construction costs for the water-gas ammonia plant were derived from actual construction costs at United States Nitrate Plant No. 1. The estimated cost of the plant using electrolytic hydrogen was largely based on the same construction costs, making due allowances and assuming that large-capacity cells would be installed.

Summarized costs per ton ammonia, 100-atmosphere plant.

	From water-gas hydrogen.	From electrolytic hydrogen.
Rated capacity, annual (tons)	11,000	11,000
Investment per annual ton	$500	$400
Cost of buildings	950,000	650,000
Cost of cells		900,000
Cost of other equipment	4,550,000	2,850,000
	Per ton ammonia.	*Per ton ammonia.*
Operating materials:		
Coke, at $6 per ton	$15.00	
Steam, at $0.85 per ton	8.50	$2.13
Water, at $0.125 per M cubic feet	3.28	1.56
Catalysts	4.68	4.40
Miscellaneous	1.00	1.00
	32.46	9.09
Process labor:		
Supervision and administration	3.29	3.29
Gas generation	5.13	1.60
Process	16.23	9.56
	24.65	14.45
Power, at $0.004 per kilowatt-hour:		
Operation	16.05	9.75
H_2 and N_2 generation	.58	60.80
	16.63	70.55
General works expense:		
Labor	12.90	12.65
Supplies	6.85	5.65
	19.75	18.30
Repairs and maintenance:		
Buildings	1.75	1.18
Electric cells		1.63
Equipment	20.70	12.95
	22.45	15.76
	115.94	128.15
Contingencies: 10 per cent of above totals	11.59	12.81
Interest, depreciation, amortization, taxes, etc.:		
Buildings	12.35	8.46
Cells		12.30
Equipment	82.70	51.80
	95.05	72.56
Grand total	222.58	213.52
Cost per pound	.111	.107

The above calculations for the consumption of operating material have been based upon experience at United States Nitrate Plant No. 1 during the trial operation and on engineering experience in related processes to-day.

Labor charges were developed by means of a complete organization chart for operation with both water-gas hydrogen and electrolytic hydrogen. The general works expense, which includes administration, general charges, etc., was developed in the same manner.

The preceding estimate for operation with electrolytic hydrogen assumed the installation of 10,000 ampere cells, which, in comparison to standard cells for the same production of gas, represents a decreased investment of approximately 1 to 4. Thus the initial investment for a synthetic process utilizing electrolytic hydrogen would be smaller than for one utilizing water-gas hydrogen, with its necessary elaborate purification apparatus. Maintenance and repair costs for electrolytic cells, as well as depreciation and overhead costs would be of a much smaller order than for water-gas purification apparatus, and, in addition, the operating-labor cost would be greatly reduced. The increased power consumption for the electrolytic hydrogen process as compared to the water-gas process may be completely or more than offset by the decreased investment and maintenance charges, together with the decreased labor and operating costs for the electrolytic production of hydrogen.

The power charge in the comparison between water-gas and electrolytic hydrogen processes is of the utmost importance, since for the water-gas ammonia process the power consumption is small, a little more than 4,000 kilowatt hours per ton of ammonia, while the consumption for the electrolytic hydrogen ammonia process is a little more than 17,000 kilowatt hours per ton. The following table indicates the costs of ammonia per pound when power rates are taken at 3, 4, 5, and 10 mills per kilowatt hour.

c. Ammonia costs at varying power rates.—

Power rate per kilowatt hour.	Water-gas hydrogen process.		Electrolytic hydrogen process.	
	Power per ton ammonia.	Total cost per pound ammonia.	Power per ton ammonia.	Total cost per pound ammonia.
$0.003	$12.49	$0.109	$52.92	$0.097
.004	16.63	.1113	70.55	.1067
.005	20.80	.1160	88.15	.1180
.010	41.60	.125	176.30	.1649

Power at 5 mills will produce ammonia at an equal cost of $0.116 per pound by the use of either water gas or electrolytic hydrogen. When power is less than 5 mills, the electrolytic hydrogen process becomes the cheaper, while it becomes the more expensive when power costs are taken at more than half a cent a kilowatt hour. It is not exactly proper to compare these two processes at the same power rates since the water-gas process uses only one-fourth as much power as does the electrolytic hydrogen process. The estimates are based on motor-driven compressors, which if steam driven would reduce the power consumption in the water-gas process by about one-third, and would make it still less important as an electric power consumer. The cost of ammonia may, therefore, be taken in accordance with available power rates.

It will be seen from the above estimates that the cost per pound of ammonia produced in a direct synthetic plant utilizing water-gas hydrogen and built in America under present conditions can not be less than $0.11 per pound, which figure is based upon power rates probably lower than can be obtained for a water-gas hydrogen system, and which does not include any costs for sale and distribution of product. It may be seen, on the other hand, that the cost per pound of ammonia for a plant utilizing electrolytic hydrogen with power at 4 mills per kilowatt hour is a little more than $0.10 per pound, which figure is not too low, since an electrolytic hydrogen installation would not be utilized except in connection with a large water-power installation or where cheap off-peak power could be obtained.

In the present stage of development of the direct synthetic ammonia process an allowance of 20 per cent on equipment, including 6 per cent for interest, 1½ per cent for insurance and taxes, 7½ per cent for depreciation and amortization, 5 per cent for development and obsolescence, may be considered a low figure even when an additional 5 per cent is allowed for maintenance and repairs. The estimate may be varied to suit opinion in these matters. The preceding estimates indicate that the costs per pound of ammonia in America to-day are about twice as great as they were in Germany in 1914. This may be attributed to the fact that the German labor costs in 1914 were about one-fourth as much as present-day American labor costs, and that their material costs were much less than they are now in America. Fixed charges, however, in both countries are approximately the same under normal exchange rates.

It is too early to obtain any costs from the operation of the Syracuse plant, and no further figures are available in regard to cost of construction or operation of foreign plants.

5. General Observations.

It is evident from the foregoing estimates that for the synthetic ammonia process to be able to compete with the by-product coke-oven industry, considerable decrease in production cost must be made. A study of the costs indicates that improvements in efficiencies at different steps of the process with corresponding slight reductions in fuel, labor, or power consumption, will not in any large proportion accomplish the desired reduction, because the overhead charges are equal to at least one-half of the total production cost. Any great saving must be accomplished by the use of the by-product carbon dioxide or oxygen from the process or by a reduction in the investment costs. Some reduction in investment per unit production could be obtained by plants of very large capacities, but as long as these plants consist of multiple items of apparatus, each of comparatively small capacity, such reduction of investment cost can be only of a secondary order. Any large reduction in the investment must presuppose fundamental modification of the process as now installed, whether in Germany, in the United States, or elsewhere. Such changes must be basic in character and represent definite reduction in the quantity and consequently in the cost of equipment necessary for operation. These advantages are claimed by M. Claude in his 1,000-atmosphere process, but he must yet demonstrate the practicability of continuous operation over a long period of time.

The outstanding economic advantage in the water-gas direct synthetic ammonia process over any other process so far developed is its comparative independence of raw material, power, etc. It consumes coke and power in such small amounts that an installation may be operated in almost any community, the location of which may be dictated by considerations other than sources of raw material, power, etc. A plant of this type, wherever placed, would have practically no effect on the industrial conditions of the community, no matter how stressed they were for other reasons.

The electrolytic hydrogen direct synthetic ammonia process, on the other hand, should involve a smaller initial investment; and if the plant were placed near some source of water power, it would be completely independent of raw material and supplies. Such a plant could be erected in a much shorter time in case of an emergency than could a plant using water gas purified by the Bosch system. The preliminary or development stage of operation in an electrolytic plant would also be shorter, due to its fewer steps in purification. An ammonia plant using electrolytic hydrogen could, with an additional investment in cells and holder capacity, be made to operate on daily off-peak power, of which there should be considerable available in the United States, and which could be purchased at very low rates from hydroelectric power stations. A process using either water gas or electrolytic hydrogen with the fundamental advantages above mentioned, which other processes do not have, is particularly worthy of energetic development, because it is one of the most important and valuable steps in national defense, and at the same time it is a most useful power in industry, one which will become more and more useful, and in greater demand in this country when the price of natural nitrates increase, and when the western farmer begins to seriously realize, as the southern farmer now does, that his land requires revivification if profitable crops are to be grown.

It has been said that the development of the direct synthetic ammonia process is the greatest of chemical engineering problems. There is no reason, however, with thorough cooperation of those following and aiding in the development, why the process can not be successfully developed in this and in other countries as well as in Germany. Successful development demands such improvements or modifications as are necessary to overcome the present troublesome mechanical difficulties, and operation economically enough to compete with other methods of ammonia production.

C. ARC PROCESS.

1. Introduction.

a. Natural fixation by the arc process.—The fixation of atmospheric nitrogen, in the form of nitric acid, by the action of electrical storms takes place in nature on an enormous scale. Although the lightning discharge is probably no more efficient in the production of nitric oxide than is the commercial arc process, yet it is estimated that by this means in the neighborhool of a hundred million tons of nitrogen are fixed and carried down to the earth's soil every year by the precipitation of rain, snow, and hail. This is far greater than the amount of nitrogen used annually in artificial fertilizers. Unfortunately, however, the nitrogen fixed in this way is not returned to the earth at the time and place most convenient to man.

b. Commercial fixation by the arc process.—The commercial electric arc process for the fixation of nitrogen consists in heating ordinary air to a high temperature by passing it through an electric arc. Under these conditions a small percentage of the nitrogen is oxidized to nitric oxide. The oxide thus formed is preserved by cooling it so quickly that its decomposition, which proceeds rapidly at high temperatures but only slowly at lower temperatures, is practically inhibited. The dioxide formed by the further oxidation which takes place spontaneously at low temperature is then absorbed in water to form nitric acid.

A large amount of energy is expended in the initial oxidation step, part of which is necessary for heating the air to the reaction temperature and part of which is absorbed by the chemical reaction itself. A portion of the heat in the gas is later recovered and used for concentrating the acid and salt solutions produced, but less than 2 per cent of the electrical energy consumed in the arc furnace is present as chemical energy in the final product.

c. Course of development.—Although the process as just outlined is extremely simple, it required a century and a quarter to develop it to its present commercial state.

Many workers from the time of Cavendish to the present have considered the process and have added fragments to our existing information concerning it. Attempts toward the commercial utilization of the process were made by Mme. Lefebre in 1859, by MacDougal and Howles in 1899, and by Bradley and Lovejoy in 1902, all of which failed. It was made evident, however, by these attempts, particularly by the work of Bradley and Lovejoy, that the arcs must be spread out in order to get the best results.

The first commercially successful experiments were carried out by Birkeland and Eyde in Norway in 1903. They took advantage of the well-known phenomenon of the deflection of an arc by means of a magnetic field at right angles to it in order to spread the arc through the gas. It was found that a furnace utilizing this effect could be built in such a rugged manner and in such a large unit that its commercial application was assured. The industrial development of the Birkeland and Eyde process has been extraordinarily successful.

Many other furnaces have been suggested and tested, but only a few have been able to compete with the Norwegian type. Of these few, the Schönherr and the Pauling furnaces are the only ones actually used in large industrial plants. In the first of these furnaces a steady and very long, slender arc is maintained, while in the latter the arc is spread by a blast of air directed against it.

2. Chemistry of the Process.

a. Formation of nitric oxide.—The fundamental chemical reaction involved in the arc process is,

$$N_2+O_2=2NO \qquad (1)$$

This change is accompanied by an absorption of heat from the surroundings equal to 43,200 gram calories. Since the specific heats of the products and reactants in the system are nearly the same and vary in the same manner when the temperature is changed, this absorption of heat is practically the same at all temperatures.

If the formation of nitric oxide (NO) be considered as a purely thermal process, the equilibrium conditions may be expressed in terms of the partial pressure of the gases by the equation,

$$(P_{NO})^2=K(P_{N2})(P_{O2})$$

where K is the equilibrium constant which must be determined experimentally. K, as a function of the absolute temperature T, is given approximately by the equation,

$$\frac{\log K}{10}=1.091-\frac{9426}{T} \qquad (3)$$

The constant term in the above expression may be somewhat too large.

A consideration of equation (2) shows that the proportion of nitric oxide in the equilibrium mixture is independent of the total gas pressure, provided the ratio of nitrogen and oxygen remains constant. However, the proportion of nitric oxide depends upon the relative amounts of nitrogen and oxygen and is a maximum in a mixture of equal parts of nitrogen and oxygen at any given temperature. This equilibrium value at all practicable temperatures is about 25 per cent greater than the corresponding value for air, which is about four-fifths nitrogen and the rest oxygen.

From equations (2) and (3) it follows that nitric oxide will be present in an equilibrium mixture to the extent of 2 per cent by volume, when air is heated to a temperature of about 2,300° C., while at 3,300° C. the amount of nitric oxide will be approximately 6 per cent by volume.

The rate at which this equilibrium condition is actually attained in such a gaseous mixture will depend upon the specific reaction rate of the formation and decomposition of the nitric oxide.

The rate of change of the partial pressure of nitric oxide at any instant is given by the equation,

$$\frac{dP_{NO}}{dt} = 1(P_{N2}P_{O2}) - k_2(P_{NO})^2 \qquad (4)$$

where P_{N_2} and P_{O_2} are the partial pressure of nitrogen and oxygen at the instant in question and k_1 and k_2 the specific reaction rates of the formation and decomposition of nitric oxide, respectively.

An examination of this equation from the kinetic point of view shows, as already pointed out from the equilibrium point of view, that the process can be carried out most favorably at any given total pressure when the partial pressures of oxygen and nitrogen are made the same.

The value of k_2 in equation (4) has been experimentally determined over the temperature range 689° C. to 1,750° C. The results are approximately represented by the equation

$$\log_{10}k_2 = -8.969 + 0.005635\ T \qquad (5)$$

From equations (3) and (5) and the relation $K = \frac{k_1}{k_2}$ the following equation for k_1 as a function of the temperature is readily derived:

$$\log_{10}k_1 = -7.878 + 0.005635\ T - \frac{9426}{T} \qquad (6)$$

From these expressions the rates of formation and decomposition of nitric oxide in any given mixture can be calculated. The case of interest is air in which $P_{N2} = 0.8$ atmosphere and $P_{O2} = 0.2$ atmosphere. Substituting these values in equation (4) we obtain

$$\frac{dP_{NO}}{dt} = 0.16k_1 - k_2(P_{NO})^2 \qquad (7)$$

From which P_{NO} at any instant can be determined by making use of equations (5) and (6). If r_1 is the ratio of the pressure of nitric oxide at the time t_1 to the equilibrium pressure and r_2 is the corresponding ratio at the time t_2, then the solution of equation (7) can be given in the form

$$\ln\frac{(1+r_2)}{1-r_2} - \ln\frac{(1+r_1)}{1-r_1} = .8K^{\frac{1}{2}}k_2(t_2 - t_1) \qquad (8)$$

The interval of time (t_2-t_1) in minutes required for producing or decomposing any given proportion of the equilibrium value of nitric oxide at a definite temperature can be calculated from the above expression. For example, in the special case of pure air at 1 atmosphere pressure and 2,300° C., it will require, according to this equation, about 0.01 second for the formation of 80 per cent of the equilibrium amount of nitric oxide, while about one-half of this time will be required for 200 per cent of the equilibrium amount of nitric oxide to decompose to 120 per cent of its equilibrium value. As the temperature is increased the decomposition rate becomes very much faster than the rate of formation. From this it appears that at the high temperatures of the arc the reactions are so rapid that equilibrium conditions must almost prevail even though the air is moving through the arc at a high velocity. Moreover, if the equilibrium amount of nitric oxide is to be preserved at ordinary temperatures the gaseous mixture must be cooled with extreme rapidity. Certainly this rapid cooling must proceed down to a temperature of 1,600° C. or less, where the decomposition of nitric oxide is relatively slower. Further cooling can be accomplished more gradually without much loss of nitric oxide.

An exact calculation of the yield of nitric oxide which may be theoretically expected per unit amount of energy (kilowatt hour) supplied to the gases can not be made because the conditions which prevail in the arc are not known with sufficient definiteness. It will be interesting, however, to calculate in round numbers the yield of nitric oxide per kilowatt hour in the simple case of air heated to a temperature of 2,300° C. At this temperature, as stated before, the equilibrium concentration of nitric oxide is about 2 per cent, which is the maximum concentration obtained commercially. As seen above, the equilibrium will be obtained under these conditions in a small fractional part of a second. Evidently, energy must be supplied for heating the air from room temperature, say 20° C., to 2,300° C., as well as for the heat of reaction. Suppose the molal specific heat of air at constant pressure as a function of the absolute temperature T, to be given by the expression

$$C_p = 6.5 + 0.001\ T \qquad (9)$$

In order to get 1 mol of nitric oxide at the concentration of 2 per cent, 50 mols of air must be used; that is, an amount of energy given by the expression

$$50 \int_{20}^{2300} C_p dT + 21600 = 895{,}000 \text{ cal.} \qquad (10)$$

must be supplied per mol of nitric oxide produced. This corresponds to the production of 60 grams of nitric acid (HNO_3) per kilowatt hour, which is not far from the average commercial yield. Although the conditions in the arc are undoubtedly somewhat different from those assumed in the above calculation it shows that the processes are equivalent to heating all the gas to a uniform temperature at about 2,300° C. or over and then cooling it so that the equilibrium amount of nitric oxide is preserved.

In the above calculation it was assumed that all of the air was heated to 2,300° C. and then suddenly cooled in order to "freeze" the nitric oxide formed. Actually, this cooling is brought about by the fact that only a part of the gas flowing through the furnace is heated to the high temperature of the arc filament, and this portion is chilled by mixing with the colder part which did not enter the arc region. If we take account of this fact it is possible to obtain a somewhat better picture of the actual process occurring in the arc than that calculated above on the assumption that all the air was heated to 2,300° C. and then cooled.

Let us take the temperature of the arc filament in air to be about 3,300° C., and let us assume that only one-third of the gas passing through the furnace is heated to this temperature, while no heat is directly imparted to the remaining two-thirds. Under these circumstances the concentration of nitric oxide in the one-third of the gas which comes in direct contact with the arc will be 6 per cent, provided the equilibrium corresponding to 3,300° C. is attained. Hence, in order to form 1 mol of nitric oxide we shall have to heat 16.66 mols of air to a temperature of 3,300° C.; that is, an amount of energy given by the expression

$$16.66\int_{20}^{3300} C_p \, d\,T + 21600 = 466{,}000 \text{ cals.}$$

must be supplied per mol of nitric oxide produced. This corresponds to a production of 116 grams of nitric acid (HNO_3) per kilowatt hour. Under the assumed conditions it should further be noted that the final concentration of the nitric oxide would be reduced to 2 per cent by dilution with the unheated air, and that the final temperature of the issuing gas would be about 1,100° C. The actual process in the arc is, of course, not as simple as assumed to be, even in this latter case, and the yields per kilowatt hour and concentrations are lower than those just calculated. .

From considerations such as the above it is obvious that the temperature gradient between the arc filament and the surrounding gas should be as steep as possible. In other words, nonuniform heating of the gas is desirable. Any heat imparted directly to the cooling air is lost, so far as the reaction is concerned, and this loss results in a decreased yield.

The possibility of preheating the gas which goes into the furnace by other than electrical means, with a resultant increase in yield, has sometimes been considered. Assuming air preheated to 1,000° C. and then subjected to an average temperature of approximately 2,300° C., the yield would be about 98 grams HNO_3 per kilowatt hour, compared with the corresponding figure of 60 grams previously obtained.

It must be noted, however, that such preheating would be attended by serious difficulties. In the first place, preheating would be limited by the fact that no suitable commercial material will stand continuous heating to more than about 1,000° C. Moreover, if 1,000° C. preheating were used, it would be necessary to mix the furnace gas with cold air in order to adjust the temperature to a safe value before the air entered the boilers or coolers. Such dilution would necessitate much larger absorption apparatus, which is already an expensive part of the arc process plant.

A great deal of effort and money has been expended in attempts to increase the furnace yields, but with little success. Some of the general conclusions from this work are as follows:

The reaction which takes place in the usual electric arc furnace for the oxidation of nitrogen is primarily of a thermal character, and no electrical effects persist at the high temperatures of the arc.

The concentration of the nitric oxide in the arc filament is about 6 per cent.

The temperature of the arc filament in air is about 3,300° C., in pure oxygen about 3,600° C., and in pure nitrogen 3,000° C.

The best yield for the Birkeland and Eyde furnace at 1 atmosphere gas pressure is about 72 grams HNO_3 per kilowatt hour, corresponding, apparently, to about 75 per cent efficiency. This yield could presumably be increased by enriching the air with oxygen and thus favoring the equilibrium, or by increasing the temperature of the arc, which in turn can be done by adding oxygen and increasing the gas pressure. None of these effects is at present used in any commercial installation.

Over a considerable range of concentration water vapor in the air acts merely as a diluent and its effect on the yield can be predicted from the mass action law.

b. Oxidation of nitric oxide.—The mixture of air and nitric oxide which leaves the furnace at a temperature of about 900 to 1,100° C. must be cooled to approximately 50° C. before it enters the absorption system, since the completeness of the absorption decreases rapidly with increasing temperature. During this process of cooling, which is accomplished in several steps, the nitric oxide is partially oxidized to nitrogen dioxide (NO_2) by the excess oxygen of the air. This reaction may be written

$$2NO + O_2 \rightleftarrows 2NO_2 \qquad (11)$$

and proceeds with an evolution of heat (13,900 calories per mol). The actual course of the oxidation is undoubtedly more complicated than indicated by equation (11), since the reaction is actually found to take place somewhat more slowly the higher the temperature, a fact which can only be explained on the basis of intermediate reactions. It will not be necessary, however, to go into this mechanism.

In actual practice it is found that the oxidation indicated by equation (11) begins at about 620° C. and is complete at about 130° C. However, the furnace gases are cooled so rapidly that only a small fraction of the nitric oxide is changed to nitrogen dioxide before its temperature has decreased to about 50° C. At this temperature the velocity of the forward reaction is so slow that several minutes are required for complete oxidation to take place. Usually the gases are passed through a large acid resistant chamber where the oxidation continues for a period of about 1¼ minutes before they enter the absorption system. After this time about 70 per cent of the nitric oxide is oxidized to nitrogen dioxide. Some of the remaining nitric oxide will be oxidized during its passage through the absorption towers.

It should be noted that below 140° C. some of the nitrogen dioxide will change to nitrogen tetroxide (N_2O_4). At 60° C. equilibrium between nitrogen dioxide and nitrogen tetroxide will exist when 50 per cent of the dioxide has been changed.

c. Absorption of oxides of nitrogen.—The absorption of nitrogen dioxide in water to form nitric acid takes place according to the following reversible reactions:

$$\begin{aligned} 2NO_2 + H_2O &\rightleftarrows HNO_2 + HNO_3 \\ 3HNO_2 &\rightleftarrows HNO_3 + 2NO + H_2O \end{aligned}$$

or

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO$$

represents the resultant change. The nitric oxide (NO) formed in this reaction is then reoxidized by the oxygen of the air to nitrogen dioxide, which in turn repeats the above changes.

The process of solution is also found to be influenced by the formation of N_2O_3 and its solubility in concentrated nitric acid, since it has been shown that the following reactions also take place:

$$\begin{aligned} NO_2 + NO &\rightleftarrows N_2O_3 \\ N_2O_3 + H_2O &\rightleftarrows 2HNO_2 \end{aligned}$$

As the final result of the various intermediate reactions which go to make up the solution process, it is found in practice, that when air containing 1 to 2 per cent of nitrogen dioxide is passed through water the nitric acid so formed reaches a limiting concentration of about 50 per cent at ordinary temperatures. At atmospheric pressure it is not possible to obtain a stronger acid than about 68 per cent by the continued action of nitrogen dioxide and oxygen on water.

The nitrogen dioxide in the arc gases may, of course, be absorbed more effectively by alkali than by water. For this reason, the water absorption towers of commercial plants are followed by alkaline absorption in order to recover in part the residual nitrous gases in the air.

The action of pure nitrogen dioxide on alkalies results in practically equimolecular proportions of nitrite and nitrate, as shown by the following equations:

$$2NO_2+2NaOH=NaNO_3+NaNO_2+H_2O \tag{12}$$

If, instead of pure nitrogen dioxide, use is made of a mixture of equimolecular proportions of nitric oxide and nitrogen dioxide, it is found that this behaves as N_2O_3 toward alkali, forming practically pure nitrite. Thus,

$$\begin{aligned} NO+NO_2 &= N_2O_3 \\ N_2O_3+2NaOH &= 2NaNO_2+H_2O \end{aligned} \tag{13}$$

These reactions take place rapidly as compared with (12). For this reason the reaction (12) does not predominate even though the actual concentration of N_2O_3 in the gases is very small, as is known to be the case. For these reasons it follows that a mixture of nitric oxide and nitrogen dioxide is more effectively absorbed than pure nitrogen dioxide by alkali.

In actual practice a mixture of nitrite and nitrate is usually obtained and the nitrite later oxidized to nitrate by treatment with dilute nitric acid.

In order to make the limited amount of pure nitrite which can be absorbed by the market, use is made of equimolecular proportions of nitric oxide and nitrogen dioxide in accordance with equation (13). A mixture of equimolecular volumes of nitric oxide and nitrogen dioxide may be obtained when the arc gases have attained a temperature of about 465° C. and a sufficient time has been allowed for equilibrium to be established, or when only partial oxidation has taken place at ordinary temperature. The first conditions are partially satisfied when the gases are absorbed in hot alkali, while the second condition can be maintained between the acid and alkaline towers by adjusting the absorption in the acid towers.

3. Arc Plants.

a. Types of furnace.—Birkeland-Eyde furnace: The furnace which is at present most widely known is that due to Birkeland and Eyde. In this furnace an alternating current arc is maintained between water-cooled copper electrodes which are placed between the poles of an electromagnet so that the direction of the arc is at right angles to that of the constant magnetic field. The magnetic field causes the arc to spread in semicircular form, first in one direction and then in the opposite direction, according to the direction of the current through the arc. As the arc filament elongates under the action of the magnetic field and recedes along the electrodes, its electrical resistance increases, causing the potential difference between the furnace electrodes to rise. When this potential has risen to a high enough value a new arc will strike across the short gap between the ends of the electrodes, thus leading to the immediate extinction of the long arc. This process repeats itself so rapidly that the arc appears as a thin disk of flame in a plane at right angles to the line joining the poles of the magnet.

The furnace is inclosed in a steel case so that it resembles a short, circular cylinder lying on its side. The inner surface of this cylinder is lined with fire-proof brick, leaving a cylindrical space about 6 inches deep and 6 feet in diameter, in which the arc expands. The air enters this arc region through perforations in the end brick wall and leaves through openings along the circumference of this region. The magnet is kept cool by the incoming air. The electrodes and fire-proof lining require occasional renewal.

The arcs have a stabilizing action so that a relatively small series impedance is sufficient to regulate the current through the arc, which fact results in a high-power factor.

It has been found that as the capacity of the furnaces has been increased their efficiency has also slightly increased. The yield is probably in the neighborhood of 70 grams HNO_3 per kilowatt hour, or 7.3 kilowatt years per metric ton of fixed nitrogen. The concentration of nitric oxide is about 1.2 per cent, while the amount of air necessary is about $2.2m^3$ per kilowatt hour.

Furnaces of this type, with a capacity as great as 4,000 kilowatts, are used in Norway.

The Schönherr-Hesseberger furnace: The Schönherr-Hesseberger furnace was developed almost simultaneously with the Birkeland and Eyde type, and has proved to be satisfactory for commercial installation. A considerable number of them are in use in the earlier Norwegian installations.

Essentially the furnace consists of four concentric iron tubes connected in such a way as to form a preheater for the air which enters the system. In the inner tube or reaction chamber a long, steady arc is produced between an insulated electrode near the lower end and the water-jacketed upper end of the tube which serves as a grounded electrode. The air enters at the bottom between the two middle tubes, passes up to the top, and then down around the inner tube, which it enters near the bottom through tangential openings, then passes up through the arc region and finally out along the outermost tube, producing a counterflow between incoming and outflowing gas. The air is given a rapid spiral motion as it enters the reaction chamber through the tangential openings. The arc filament assumes a central position in the tube and remains very steady. The circulation of the air around it keeps the iron tube relatively cool, although the diameter of the tube is only 6 inches or 8 inches and the power input as much as 800 or 1,000 kilowatts.

The problem of stabilizing the arc in this furnace is more serious than in the Birkeland and Eyde furnace, because there is no automatic way provided for reestablishing the arc should it be blown out. The arc is formed between the tube and insulated electrode by a special rod, which can be made to touch both simultaneously and can then be quickly removed; the spiral air current causes the end of the arc filament to move rapidly up the side of the iron tube to the water-jacketed upper end. In large commercial furnaces the arc is sometimes over 20 feet in length, so that special methods are necessary in order to kindle it.

The furnace gases have a temperature of about 1,200° C. as they leave the reaction chamber, but only 800° C. at the furnace exit, since some heat is transferred to the incoming air in the process of preheating. The concentration of the nitric oxide is about 1.8 per cent, which is somewhat higher than in the Birkeland-Eyde process, partly because less air is forced through the furnace by the compressors. The yield is about the same as for the Birkeland-Eyde furnace, although in this case there is a decrease in the yield as the size of the furnace is increased beyond a certain point.

Pauling furnace: In the Pauling furnace the arc passes between two water-cooled cast-steel tubular electrodes, which are set perpendicular to each other and in a vertical plane. The arc starts between two thin blades which are attached to the electrodes at their nearest point. The distance between these blades is regulated so that the air gap is easily broken down by the applied electromotive force. As soon as the arc is formed the strong air blast which issues up between the electrodes blows the arc filament along the divergent electrodes until it is broken. The electrodes are about 2 inches apart at their base, so that the air can pass freely between them. The blades are sufficiently thin so that they do not offer an appreciable obstruction to this motion of the incoming air. The arc has the appearance of a vertical sheet of flame extending between the electrodes. Both the electrodes and the kindling blades require very frequent renewal, which can, however, be done without much labor. The arcs operated in series are inclosed in a single fireproof furnace. In addition to the tubes below the two sets of electrodes where the air enters, there is a gas passage in the wall separating the two arcs, through which cooled furnace gas is drawn. This gas serves to cool the gas which has passed through the arc without diluting the nitric oxide. The concentration of nitric oxide is about 1 per cent or less, while the yield is probably somewhat less than in the Birkeland-Eyde furnace. The temperature of the gas leaving the furnace is about 1,000° C. This is somewhat reduced in a preheater and in a tower filled with fire brick before the gas reaches the steam boilers. When a cooling tower becomes too hot, it is cooled by drawing air through it. The capacity of the Pauling furnace is about 600 to 1,000 kilowatts.

Other furnaces: A large number of modifications of the above furnaces have been suggested, yet in most cases there is not sufficient data to demonstrate that the modifications are significant. Moscicki and Wielgolaski furnaces, which are somewhat similar to the Birkeland-Eyde and Schönherr furnaces, respectively, are actually used in several small commercial plants. The arc plants in Washington and British Columbia use the Wielgolaski furnace.

b. Recovery of product.—In all cases the nitric oxide and air mixture passes from the furnace through a fireproof brick-lined iron pipe to preheaters, steel boilers, and aluminum coolers. This cooling is thus accomplished in several steps. The cooled gas is then passed through acid and alkaline absorption towers.

The accompanying flow sheet (fig. 5), although it does not correspond to any actual case, will serve to indicate certain facts concerning the process. The plan is not greatly different from that employed in a unit of a large Norwegian plant, and as shown would have a capacity of about 25,000 kilowatts. It must be remembered, however, that the particular characteristics of the furnaces employed will determine to some extent the design of the plant. For instance, the higher concentrations of nitric oxide obtainable from the Schönherr furnace would result in a smaller absorption system than that of a Birkeland-Eyde plant. Further, the flow sheet shows that in case of emergency certain parts of the plant could be shut down without overloading other parts unduly. The actual amount of such overloading which could be permitted is, of course, a question of engineering design.

The water vapor originally in the air, or that due to boiler leaks. may cause appreciable amounts of acid to be formed, thus leading to corrosion of the boiler. This is reduced to a minimum, however, if

ARC PROCESS FLOW SHEET.
(REPRESENTING ONE TYPICAL UNIT)

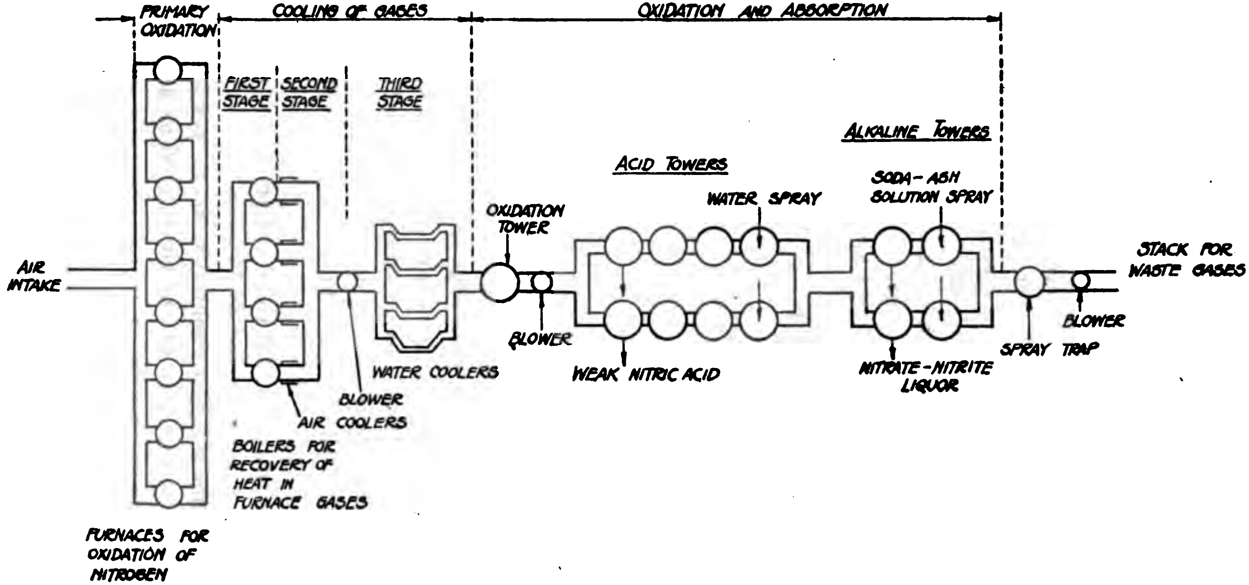

FIGURE 5

the temperature is not allowed to fall to a point where appreciable NO_2 is formed. The air coolers which are shown as preheaters serve to heat the cold gas which enters the furnace and at the same time greatly reduces the chances for corrosion in the steam boilers, because with this arrangement the temperature of the gas before it leaves the boilers can be kept considerably above the point where oxidation of the nitric oxide is appreciable. When the gas has attained the temperature where acid may be formed, it is passed through aluminum tubes which are immersed in water. Even the aluminum is attacked by nitric acid under favorable circumstances, so that leaks which would allow water to enter the cooler must be strictly eliminated.

Table I gives the temperature change in the different parts of the process as well as the gas pressure drop and the time of the gas in each section. These figures would apply approximately to a Birkeland-Eyde plant.

TABLE I.

Section.	Temperature of gas.	Pressure drop.	Time of gas in section.
	°C.	*Inches water.*	*Seconds.*
Furnaces	25–1,100	5.4	2
Boilers	1,000– 300	4	30
Preheaters	300– 175	2.5	
Aluminum coolers	175– 40	7	
Oxidation	40– 56	1	75
Acid absorption	56	17	190
Alkaline absorption	56	7	90

The pressure drop in the various sections is maintained by powerful blowers which may be placed as shown on the flow sheet. Since 70 per cent of the nitric oxide is converted into NO_2 by the time the gas enters the absorption system, and 4 per cent of the total nitric oxide is lost through the stack, the gas will contain enough acid to cause corrosion of the blowers unless they are sufficiently acid resistant.

The oxidation tower is acid resistant and large enough so that the gases remain in it for a period of 75 seconds. For a Birkeland-Eyde system this volume is approximately 0.005 m^3 per kilowatt of furnace capacity. This section can not be considered as an absolutely essential one since the absorption system is generally capable of recovering the fixed nitrogen even though the degree of oxidation of NO to NO_2 as the gas enters the acid towers is not as great as 70 per cent. The alkaline absorption can easily compensate for the decreased acid absorption, so that the loss would merely be the difference in the value of the product as nitric acid or sodium nitrate or nitrite.

The absorption system consists of brick or granite towers about 20 feet in diameter and 75 feet high. These are filled with broken quartz over which the water or alkaline solution trickles in countercurrent manner as the gas passes up through them. The relative number of acid and alkaline towers will, of course, be determined by the nature of the product desired. In the case illustrated on the flow sheet, 85 per cent of the fixed nitrogen is absorbed as acid and 15 per cent as sodium nitrate or nitrite. This is about the maximum amount of the product which could be economically recovered as acid. Pumps may be used for circulating the alkaline solution while the acid is raised from one tower to another by compressed air lifts.

In Table II approximate values of the energy changes in the various sections of a Birkeland-Eyde plant are given in terms of the energy supplied at the electrodes of the furnace.

TABLE II.

Section.	Energy received.	Energy given out.
Furnace	100 consumed in arc, 2.6 in gas, 0.4 in magnet windings.	10 as radiation, 6 in electrode water, 87 in gas.
Boilers	85 in gas, 7 in feed water	3 as radiation, 72 in steam generated, 17 in gas.
Preheater	16.8 in outgoing gas	2.6 to incoming gas, 14.2 in gas.
Aluminum coolers	14 in gas	8 to cooling water, 6 in gas.
Oxidation	6 in gas	
Acid concentration	4.5 in acid, 25 in steam made above.	28.3 in vapors driven off, 1.2 in acid.
Alkaline concentration	1 in nitrate and nitrite, 9 in steam made above.	9.7 in vapors driven off, 0.3 in sodium nitrate.
Auxiliary apparatus	4	0.2 blowers, 0.4 magnets, 1.6 other auxiliaries.
Steam from boilers	75	40 steam turbines, 33 concentration, 2 boiler pumps.

From this it is evident that only a very small part of the total energy delivered to the furnace is converted into chemical energy. For this reason the arc process has been forced to locations where power is cheap.

Although sufficient information for a complete description of any commercial arc plant is not available, nevertheless it will be instructive to note the general tendency in arc process practice as manifested in the Norwegian plants. The plants are situated near Christiana and all the power is obtained from a single river where the power developments have been exceedingly cheap.

Starting with 3-horsepower experiments in 1903, and a 150-horsepower plant in the same year, the Norsk-Hydro Co. has developed as follows:

1904, 2 furnaces of 1,000 horsepower each near Arrondel.
1905, 2,500 horsepower at Notodden.
1907, 40,000 horsepower at Notodden.
1911, 55,000 horsepower at Notodden.
1919, 60,000 horsepower at Notodden.
1911, 145,000 horsepower at Rjukan I.
1916, 145,000 horsepower at Rjukan II.

This rapid expansion is evidence of the fact that the Norsk-Hydro Co., which owns and operates the plant, has been a great financial success. The published accounts of the company seem to indicate that the capital stock, which has been increased manyfold since the beginning, is practically covered by reserves which have been built up even while the debts of the company have been amortized more rapidly than was anticipated. The guaranteed interest on preferred and common stock has always been paid, and in 1918 both stocks received 12 per cent. This was, of course, due to the prosperity caused by the war. Since 1905 most of the capital has been controlled by Norwegian interests. It was about at this time that the Germans became interested in the development of the Haber process, and for this reason most of their capital in the Norsk-Hydro Co. was withdrawn.

The total output of the company is over 30,000 metric tons of fixed nitrogen per year. Most of the product is in the form of calcium nitrate made by treating limestone with the dilute acid from the towers. Ammonium nitrate and sodium nitrite and nitrate are also produced. The nitrite market is so limited, however, that most of the alkaline tower product is converted to nitrate. The greatest part of the product is consumed in Norway as fertilizer and is sold as Norwegian saltpeter. The company owns and operates its own railroad, wharves, and warehouses on the seacoast.

The electrical current used is in all cases 3-phase, 50-cycle at 10,000 volts. At Notodden, Schönherr, and Birkeland-Eyde furnaces have been installed and developed simultaneously. In Rjukan I there are 96 Schönherr furnaces of 800-kilowatt capacity each and 6 Birkeland-Eyde furnaces of 3,500-kilowatt capacity each. In the later development at Rjukan II all the 36 furnaces are Birkeland-Eyde of 4,000 kilowatts each. The condition of the patent rights of the Schönherr furnace may be partly responsible for the abandonment of the furnace in this installation.

At Rjukan II the 10 turbogenerator sets, 2 steam-generator sets, and 36 furnaces are all in one large permanent building. The gas is piped in 8 or 10 aluminum pipes 3 feet in diameter to a place about three-fourths of a mile along the river. Here are 60 granite absorption towers, each over 20 feet in diameter and 75 feet high, and all inclosed in a single permanent building. The aluminum pipe lines serve both as a cooler and oxidation plant. The steam used for evaporation and concentration purposes is also piped the entire distance of three-fourths of a mile.

Other arc process plants are situated as follows:

Place.	Type of furnace used.	Capacity, in tons, of fixed nitrogen per year.
1. Rjukan and Notodden, Norway	Mostly Birkeland-Eyde; some Schönherr	30,000
2. Bodio, Switzerland	Moscicki	700
3. LaRoche de Rome, France	Pauling	1,300
4. Pierefitte, France	Birkeland-Eyde	
5. Lepecq, France	Guye	(1)
6. Legano, Italy	Variation of Pauling	1,200
7. Near Rome, Italy		
8. Patsch, Austria	Pauling	4,000
9. Muldenstein, Germany	Birkeland-Eyde	
10. Seattle, Wash., U. S. A.	Wielgolaski	300
11. Vancouver, B. C.		800

[1] Experimental plant.

It is impossible to give complete data concerning the capital cost and operating expenses of any arc plant. An approximate estimate on a Birkeland-Ryde unit of about 25,000 kilowatts may be of interest. It must be remembered, however, that any such estimate is dependent upon so many conditions that strictly such figures can only be significant when all these factors are definitely known and considered. In Table III the percentages of capital cost of the chemical plant and its operating expense is given opposite each section of the plant. The power plant or power costs are not included. Also the costs of concentration and conversion processes are not included.

TABLE III.

Section of plant.	Per cent capital cost.	Per cent total operating expense.	Section of plant.	Per cent capital cost.	Per cent total operating expense.
Furnace	23	35	Acid absorption	35	15
Boilers and preheaters	8	7	Alkaline absorption	8	15
Coolers	2	6.5	Blowers, etc	4.5	7
Oxidation	1.5	2	Miscellaneous	19	12

The capital cost per ton of fixed nitrogen per year could under most conditions be covered by $700, while the operating expense, excluding power, would probably be approximately $100 per ton of fixed nitrogen per year. Thus, if 12 per cent capital charges is added to the operating expense, the cost of dilute nitric acid would be $184 per ton of nitrogen, exclusive of power. If the yield be taken as 7.3 kilowatt years per metric ton of nitrogen, it will be seen that power charges will equal all other charges if the power costs $24 per kilowatt-year.

D. THE CYANIDE PROCESS.

1. Description of Process.

a. Introduction.—The process for the fixation of atmospheric nitrogen in the form of cyanide consists essentially in heating to an elevated temperature a mixture of the carbonate of an alkali or alkaline earth metal with carbon in the presence of nitrogen gas. The product is a crude cyanide usually containing from 5 to 10 per cent of nitrogen, depending on the nature and composition of the charge, and can either be treated to produce a marketable form of cyanide or subjected to the action of steam to produce ammonia. In either case the residue can be used again in the process.

Researches on the synthesis of cyanides date back to at least 1784. About that time Scheele discovered that potassium cyanide could be made by heating a mixture of potassium carbonate and carbon to a high temperature in the presence of nitrogen. Numerous investigations on the synthesis of cyanides have since been made, but the reactions involved are so complex that they are still not fully understood. In the various investigations all of the common alkali and alkali earth carbonates have been studied, but only sodium and barium carbonates are now generally regarded as suitable for cyanide synthesis from an economic as well as a chemical standpoint.

In spite of the many attempts which have been made in Great Britain, France, this country, and elsewhere to establish the cyanide process on a commercial scale, its successful operation still remains to be accomplished. In connection with the appraisal of its commercial possibilities, however, it should be remembered that the process might be successfully operated to produce cyanide, in which the nitrogen has a comparatively high value, and still be commercially unsuccessful for the production of the much cheaper ammonia.

The process involving the use of barium carbonate has been quite extensively investigated in Great Britain, but as far as is known no studies of any consequence have been made on it in this country. The barium cyanide process is briefly described in another section of this chapter ("Other Fixation Processes," E 5).

Revival of interest in the sodium cyanide process in recent years as a nitrogen fixation possibility is due largely to the investigations of J. E. Bucher. His results are embodied in a series of United States and foreign patents beginning in 1914, and a summary of his investigations was published in 1917.[36]

The particular method which Bucher proposed for carrying out the process on a commercial scale has become known as the Bucher process, also commonly referred to in this country as the cyanide process. This process consists in briquetting an intimate mixture of finely divided sodium carbonate (soda ash), carbon, and iron; feeding the dried briquets into an externally heated, vertical retort in which the charge reacts with nitrogen at about 1,000° C. to form sodium cyanide; and then leaching the cooled product to obtain the cyanide or subjecting it to the action of steam to produce ammonia. The residue in either case is used again in the process.

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[36] J. Ind. and Eng. Chem., 9: 233 (1917); see also U. S. Patent No. 1,091,425.

The commercial development of this process in this country was undertaken by the Nitrogen Products Co., who erected experimental plants at Saltville, Va., and at Greene, R. I. In 1918 the United States Chemical Plant No. 4 (hereinafter referred to as U. S. C. P. No. 4) was constructed at Saltville, Va. The general plan of this plant was similar to that of the Saltville plant of the Nitrogen Products Co. and was designed to produce 10 tons of sodium cyanide per day. A description of this plant and process has been published.[87] The plant had been in operation only a few weeks when the war ended, and it has since been scrapped. During 1918 investigations on different phases of the process on a semicommercial scale were carried on by the Nitrate Division in the experimental plant of the Nitrogen Products Co. at Greene, R. I.

The Air Reduction Co. has developed a modification of the cyanide process differing from the Bucher process principally in that (1) a much smaller proportion of iron is used in the charge, (2) a revolving retort slightly inclined to the horizontal is used instead of the vertical retort of the Bucher process, and (3) the charge is not briquetted. A test run of this process was observed in 1918 by representatives of the Nitrate Division.

The principal advantages which have been claimed for the cyanide process are: (1) Low temperature as compared with the arc and cyanamide processes, permitting the direct use of fuel instead of electrical energy and resulting in lower furnace-upkeep costs; (2) low fuel requirement; (3) comparatively inexpensive and abundant raw materials; (4) simplicity of process and hence low capital outlay; and (5) location less limited than the other fixation processes. That the process in its present state of development falls far short of the ideal cyanide process—one embodying all of the features enumerated above—will be seen from the following discussion.

Although the cyanide process is still in the developmental state, it has received and is receiving so much attention in this country that it seems desirable to treat it more fully in this report than its present commercial importance might warrant.

b. Chemistry of the process.—The chemistry of the cyanide formation, a combining of sodium carbonate (soda ash) with carbon and nitrogen to form sodium cyanide, may be summarized by the equation

$$Na_2CO_3+4C+N_2+\text{iron}=2NaCN+3CO+\text{iron}-138{,}500 \text{ cal.} \quad (1).$$

The reaction begins at about 900° C., or slightly lower, and is quite rapid at 1,000° C. The upper temperature limit is about 1,100° C. It is believed that at this temperature the iron then begins to decompose the sodium cyanide, the reaction being the same as in the case-hardening of metals by sodium cyanide.

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[87] Maj. Chas. O. Brown, J. Ind. Eng. Chem., 11: 1010 (1919).

The thermal relations involved in the process are particularly important. The equation shows that a large quantity of heat is absorbed in the formation of sodium cyanide. Nevertheless, if it were possible to return to the process the heat of combustion of the carbon monoxide (CO) formed, there would be a positive heat balance of about 32,500 calories per mol of sodium cyanide, and hence the process could be regarded as exothermic. It is not possible, however, to burn the carbon monoxide in the reaction mass since sodium cyanide is oxidized more readily than the carbon monoxide.

That the presence of finely divided iron in the charge promotes the formation of sodium cyanide has been quite definitely established. The reaction occurs with appreciable velocity at 1,000° with iron in the charge. A much higher temperature is required without iron, leading to loss of alkali, destruction of retorts, and high fuel consumption, which were the factors causing failure in the earlier attempts. The manner in which iron acts to catalyze the formation of sodium cyanide has not been clearly demonstrated. It is known that iron catalyzes the reduction of sodium carbonate to metallic sodium, which may be an intermediate step in the formation of sodium cyanide. According to Bucher, iron is also required to bring about the reaction of metallic sodium with carbon and nitrogen.

Sodium cyanide is destroyed by appreciable quantities of oxygen, carbon dioxide, or water vapor. It is, therefore, necessary to carry out the reaction under reducing conditions, and consequently it is not possible to furnish the heat required for the reaction by combustion within the mass of the charge.

The effect of carbon monoxide, CO, on the reaction is a matter of some doubt. Since carbon monoxide is one of the products of the cyanide-forming reaction, it is to be expected that the percentage of sodium cyanide in the liquid melt of sodium carbonate and sodium cyanide, would be lowered by increasing the CO concentration. We have, however, no means of predicting the extent of this influence. Moreover, the actual relations existing in the reacting charge are probably so complex, and so little is known as to the exact compounds present during the reaction, and as to the mechanism of the reaction, that it is difficult to state with certainty the exact influence of any factor on the conversion. It appears from the study of Ferguson and Manning[38] that the maximum yield of cyanide is in fact materially reduced by the presence of CO in the nitrogen. According to their results, the maximum possible conversion should be less than 35 per cent at 950° C. and about 60 per cent at 1,000° C. with producer gas. On the other hand, Bucher and other workers have claimed high conversion of sodium carbonate to sodium cyanide using producer gas which normally contains about 33 per cent CO and 67 per cent N_2.

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[38] J. Ind and Eng. Chem., 11: 946.

c. Raw materials.—A commercial grade of sodium carbonate (soda ash) may be used in the process. This material is a common article of commerce and is manufactured in very large quantities. This point is not of special importance in the cyanide process if operated to produce ammonia, since in that case the sodium carbonate would be regenerated and used over and over, additional carbonate being required only to replace mechanical losses. From the standpoint of producing sodium cyanide, however, it is very important that the process depends upon a material the supply of which is abundant and dependable. By way of contrast it may be noted that the manufacture of sodium cyanide by the Castner-Roessler process, which is the one now in commercial use, depends on the supply of metallic sodium which is not a common article of commerce.

The selection of the form of carbon which is the most suitable for use in this process involves many questions. Equation (1) shows that about one-half pound of carbon is required per pound of sodium cyanide formed. For each cycle of operations through which a given charge passes this amount of carbon must be supplied. It is evident that all impurities accompanying this carbon accumulate in the charge, so that the same charge can not be used indefinitely unless an ashless form of carbon is supplied. Therefore we may either use coke having considerable ash and discard some material at intervals, or supply the more expensive comparatively ashless carbon and use the same charge practically indefinitely. The choice between these alternatives can be made only on the basis of a full knowledge of the technical suitability, price, and supply of the different kinds of carbon and of the cost of recovery of soda ash and iron from the discarded coke.

Metallurgical coke, petroleum coke, and pitch coke have been tried in the various investigations of the cyanide process. So far as is definitely known, there are no technical disadvantages in the use of metallurgical coke other than the necessity of discarding materials at intervals in accordance with the first of the alternatives mentioned above. The usual ash content is 10 to 15 per cent. It is available in very large quantities in all manufacturing communities at about $4 per ton in normal times. Although petroleum coke is quite satisfactory technically—having only 1 to 2 per cent of ash, most of which is iron oxide and therefore not objectionable—the supply would probably be inadequate to meet the demands of large-scale ammonia manufacture by the cyanide process. Pitch coke is practically ashless, and from that standpoint would be ideal for use in this process. Difficulty was experienced at the U. S. C. P. No. 4 in obtaining strong briquettes from charges containing pitch coke. It is claimed, however, that this difficulty has now been overcome. Statistics on the production of pitch coke are not available, but it is probably more plentiful than petroleum coke.

Assuming that about 1½ pounds of carbon is used per pound of ammonia, the cost of carbon, if a practically ashless form was used, would be about $0.011 per pound of ammonia, assuming a cost of $15 per ton, the present price of petroleum coke.[39] The rate of accumulation of impurities would be quite slow. On the other hand, although metallurgical coke can be obtained at a much lower cost it is not possible, according to a rough calculation, to pass a charge in which the carbon is introduced as metallurgical coke more than four to eight times before discarding the coke. These observations are offered as examples of the sort of considerations which would determine what kind of carbon should be employed.

It has been suggested that if coke containing a considerable amount of ash is used, the last run before the coke with accumulated impurities would normally be discarded could be made to yield cyanide as the final product instead of ammonia, thus avoiding the extra expense of recovering soda ash from the contaminated charge. This would be particularly desirable in case of high conversion to cyanide. If the success of the cyanide-ammonia process were dependent on such a practice, however, the size of the industry would be limited by the demand for sodium cyanide, which is small as compared with that for other forms of fixed nitrogen.

The iron required to catalyze the reaction may be supplied as powdered cast iron, as iron oxide scale, or in any other relatively pure form which is sufficiently cheap. If ashless carbon is used in the charge, it will be necessary to add only a small amount of iron to replace mechanical losses. If the carbon is supplied as ash-containing coke, however, additional iron may possibly be required, since it may be more economical to discard the iron with the contaminated coke than to recover it. This would be determined by the cost of iron as against the cost of recovery.

The only other raw material is nitrogen. Whether this must be supplied as practically pure nitrogen or whether a mixture of nitrogen and carbon monoxide, made by simply passing air through heated coke, can be used, is not definitely known. It seems probable that pure nitrogen is preferable and perhaps essential. At any rate, since nitrogen can be produced very cheaply from liquid air, this is a matter of no great importance unless the use of producer gas is attended by some other advantage than the elimination of the cost of nitrogen. For example, it has been suggested by John Dix Morgan that the charge might be heated by passing hot producer gas (33 per cent CO, 67 per cent N_2), coming directly from the producer, through the charge. This proposal is considered later in the discussion of nitrification.

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[39] Chem. and Met. Eng. 24: 1082.

d. Composition of charge.—In carrying out the reaction between soda ash, coke, and nitrogen in the presence of iron, the proportions used, the manner of handling the charge, and other particulars have varied considerably in the different attempts. All are alike, however, in having used a large excess of coke, and most workers have favored the use of considerable quantities of iron. The charge which was used in most of the runs of the U. S. C. P. No. 4 at Saltville, Va., is perhaps typical, except that the iron content was somewhat lower than that sometimes recommended. The proportions were about 30 per cent Na_2CO_3, 55 per cent coke, and 15 per cent iron. The charge used for most of the experiments on the Air Reduction Co.'s process was 43.4 per cent Na_2CO_3, 53.1 per cent coke, and 3.5 per cent Fe_2O_3.

e. Preparation of the charge.—In all modifications of the cyanide process it is necessary to have the materials more or less finely ground, both the coke and the iron usually being required to pass a 100-mesh sieve. An intimate mixture of the constituents is obtained by dry mixing and finally kneading with sufficient water to give the mass the consistency of stiff dough.

In any process similar to that used at Saltville, it is necessary to briquet the charge in order to facilitate the movement of material through the retorts and to prevent channeling in the charge with resultant lack of contact with nitrogen. Bucher recommended mixing the charge with hot water, forming the briquets, and then allowing them to cool below 35° C., under which conditions the formation of the hydrate $Na_2CO_3.10H_2O$ would cause the briquets to set and become hard. In the operations at U. S. C. P. No. 4, however, the briquets were sent directly while hot to the driers so that briquets were formed without the formation of the hydrate. In fact it seems probable that the formation of $Na_2CO_3.10H_2O$ is to be avoided, due to the tendency of the briquets to crumble when the water of hydration is expelled. The hot briquets were dried at U. S. C. P. No. 4 at about 150°; an even higher temperature would have been desirable in order to hasten the drying.

The size of the briquets is important. A small briquet favors a rapid absorption of nitrogen, while a large briquet has the advantage of reducing the sticking and packing of the charge during treatment. In general, it may be said, however, that with reasonably small briquets the rate of heat penetration rather than nitrogen penetration is the factor which largely determines the time required for treatment of a charge in any apparatus which has been developed to date so that the second consideration is the more important. The size of these briquets is usually between one-eighth inch and three-eighths inch in diameter and 1 inch and 3 inches in length.

In the process of the Air Reduction Co., the charge is prepared by heating the mixture with water, drying, and sintering at medium red heat, thus producing a product which, while largely in the form of a relatively fine powder, has all of the constituents in permanent contact. The charge is then nitrified in a revolving nichrome tube, inclined slightly to the horizontal, and which is externally heated. Channeling is thus prevented in spite of the fact that the charge is powdered.

f. Nitrification of the charge.—The next step after the preparation of the charge is the treatment with nitrogen at about 1,000° C. It is in this connection that some of the gravest difficulties are encountered. At the reaction temperature the charge tends to become a semiplastic, somewhat sticky mass. This material must be handled in such a way as to make the nitrification practically continuous if large quantities are to be treated efficiently. The charge can not be heated by a direct flame, because of the action of oxygen and carbon dioxide on sodium cyanide. Hence, if the heat required is to be furnished by burning fuel, it can be done only by external heating of retorts containing the charge or perhaps by hot gases passing through the charge. Externally heated retorts, to have the necessary properties of high heat conductivity, must be made of some metal. This necessary feature gives rise to the problem of protecting the retorts from oxidation in the free flame.

It has been suggested that if the presence of carbon monoxide in the nitrogen is not deleterious some of the difficulties attending the heating of the charge might be avoided by supplying the heat required by passing through the briquetted charge the hot gases coming directly from a gas producer blown with air only. Such a gas would contain approximately 33 per cent CO and 67 per cent N_2. Such a method would without doubt give a very much longer life to the retorts and would overcome the difficulty of getting heat into the relatively nonconducting charge. It will be noted, however, that less than one-third of the total calorific value of the coke goes into the gases, since the coke is only burned to CO. Furthermore, since in general the endothermic reaction takes place through a relatively limited temperature range—say, 850° to 1,100° C.—enough gas must be supplied to give out, in dropping through that temperature range, all the heat required for the reaction. For a typical charge only a comparatively small amount of the sensible heat of the gases leaving the reaction zone would be required to bring the descending charge to the reacting temperature. The gases would, therefore, still contain a considerable portion of their sensible heat upon leaving the retort. From the above consideration it appears that the proposed method of heating is inherently very wasteful of coke. A rough calculation indicates that the cost of coke for heating by this method would be in the neighborhood of $0.03 or $0.04 per pound of ammonia with coke at $4 per ton. If such a cyanide-ammonia plant could be combined with some other plant which could effectively utilize the sensible heat and the high calorific value of the gases from the retorts, the cost for fuel chargeable to ammonia might, of course, be very greatly reduced.

In the usual form of the cyanide process, the retorts are metal pipes surrounded by an oil or gas fired furnace and provided with a gas-tight mechanism for continuously discharging the treated briquets at the lower end. This is the type which was used at U. S. C. P. No. 4. The use of this type necessitates the briquetting of the charge to minimize the sticking of the charge on the walls of the retorts and to facilitate ready access of nitrogen to all parts. In spite of the use of briquets, the retorts very frequently become clogged. This is a difficulty which has been encountered in nearly every attempt to operate the cyanide process. The work at U. S. C. P. No. 4 did not continue long enough definitely to establish the remedy for this trouble. It was observed, however, that the sticking was less serious in runs where the charge contained lower alkali. The impression was also gained that the character of the ash in the coke used in the charge influenced the feeding qualities, the acid-soluble portion of the ash apparently aiding the feeding qualities.

In all commercial tests of the cyanide process about which we have information, the formation of cyanide is much less rapid than we might have expected from the statements of Bucher and others, who have claimed that the absorption of the nitrogen is very rapid when the charge has reached the proper temperature. This is presumably due to the low heat conductivity of the material, with consequent slow rise in temperature through the mass. From the figures given on the U. S. C. P. No. 4 for the rate of delivery of cyanized product from the retorts (45 pounds per hour), the density of the product (57.5 pounds per cubic foot), and the dimensions of the retort (8 inches by 8.66 feet), it is calculated that the charge required about four hours to pass through the heated zone of the retort in the runs which gave the best results. The conversion of Na_2CO_3 to NaCN under these conditions was about 50 per cent. For shorter periods of heating the conversion dropped off rapidly. The total time for passage of material through the heated zone of the Air Reduction

Co.'s retorts was 15 to 22 hours. The conversion was about 45 per cent.

It is evident that long heating results not only in low plant capacity and high labor costs but is also one of the factors contributing to the very low heat efficiencies which have been obtained. The thermal efficiency at U. S. C. P. No. 4 was about 6 per cent.

The nitrogen efficiency—that is, the ratio of the nitrogen absorbed to that supplied—is low, being about 17 per cent both at U. S. C. P. No. 4 and at the Air Reduction Co.'s plant, as calculated from the rates at which nitrogen was supplied and cyanide formed. At U. S. C. P. No. 4, for example, the nitrogen flow was 2½ cubic feet per minute to each retort, and under the best conditions 7 pounds of sodium cyanide were formed per retort hour. A low nitrogen efficiency is perhaps to be expected, since according to the equation

$$Na_2CO_3+N_2+4C=2NaCN+3CO$$

3 volumes of carbon monoxide, CO, appear where 1 volume of nitrogen, N_2, is absorbed. The rate at which cyanide is formed is thus decreased by dilution of the nitrogen gas, and probably the maximum possible conversion is lowered due to the effect of CO on the equilibrium content of sodium cyanide. When the nitrogen efficiency is 17 per cent it is calculated that the gases from the retorts have a composition by volume of about 38 per cent CO and 62 per cent N_2.

The cyanized material is usually discharged from the retorts into containers in which an atmosphere of nitrogen is maintained, since contact of the hot charge with air results in the oxidation of some cyanide to cyanate and probably some to carbonate with loss of combined nitrogen.

g. Production of ammonia from crude cyanide.—Ammonia has not yet been made in any quantity by the cyanide process, although the reaction by which cyanide yields ammonia has long been known. In 1918 investigations were made by Nitrate Division representatives on a semicommercial scale in the laboratories of the Nitrogen Products Co. at Greene, R. I., and at the plant of the Air Reduction Co. at Jersey City, N. J. The products of the reaction are sodium formate and ammonia, except when the hydrolysis is carried out at temperatures of 400° to 500° C. or higher, in which case the sodium formate is decomposed to sodium carbonate, hydrogen, and carbon monoxide. The production of ammonia from crude cyanide by the action of steam at lower temperatures may be represented as follows:

$$NaCN+2H_2O=NaHCO_2+NH_3+64{,}000 \text{ cal.} \qquad (3)$$

Some sodium cyanate may sometimes be present. This compound is also readily hydrolized:

$$2\ NaCNO+3\ H_2O=Na_2CO_3+2\ NH_3+CO_2+15{,}340\ \text{cal.} \quad (4)$$

The presence of finely divided iron in the product complicates the process by the tendency to form sodium ferrocyanide according to the equation:

$$6\ NaCN+Fe+2\ H_2O=Na_4Fe(CN)_6+2\ NaOH+H_2 \quad (5)$$

In studies of the steaming of cyanized briquets at *atmospheric pressure* at Greene, R. I., it was found that to get a practically complete liberation of the combined nitrogen it is necessary to raise the final temperature to 650° to 700° C. The best yields were obtained when the temperature was increased gradually from 250° to 650° as the reaction proceeded. The heat of the reaction supplied the heat during the first part of the hydrolysis, but it was necessary to apply external heat to obtain the required final temperatures. The iron in the briquets was completely oxidized under these conditions. The formation of ferrocyanide in the briquets proceeded below 450° C., but above that temperature this compound was hydrolyzed, yielding ammonia. A 100 per cent yield of ammonia was obtained in a few cases, but it is doubtful whether it would be practicable to get more than 85 to 90 per cent yield, since the last 10 to 15 per cent came off slowly and only at a quite elevated temperature, as noted above.

A study of the hydrolysis of sodium cyanide, sodium ferrocyanide, and of cyanized briquets containing the iron of the charge under various conditions as to temperature and pressure was made by the research staff at U. S. C. P. No. 4 in 1918 and 1919. It appears from their results that it would be possible to hydrolyze sodium cyanide in the presence of iron without serious ferrocyanide formation, provided the proper conditions are observed. They found that with dry steam at 300 pounds pressure—corresponding to a temperature of about 220° C.—the amount of ferrocyanide in the cyanized briquets was sometimes even decreased. It was indicated that a yield of ammonia at least 90 per cent of the theoretical could be expected under these conditions. It appears that hydrogen was not usually found in the gases coming from the autoclave. Hence there was no oxidation of the iron in the briquets.

The apparent advantages of the pressure hydrolysis are (1) a lower temperature and (2) avoidance of oxidation of iron. If the briquets are to be disintegrated after hydrolysis for re-forming into new briquets, the second point is perhaps not of special importance, since under the usual conditions the iron is largely oxidized in making up and drying the briquets. The disadvantages inherent in pressure apparatus must be considered in choosing between the two types of hydrolysis. It may be found that with steam under pressure the reaction may go to completion using only the heat of the reaction, thus dispensing with apparatus for supplying external heat. Although this has not been demonstrated, there are some reasons to believe that it may be possible.

The residue remaining after hydrolysis containing sodium formate (or sodium carbonate), carbon and iron may be used for the formation of another batch of cyanide, either directly or after powdering and adding carbon to replace that used up. After a certain number of cycles, the number depending on the amount and character of impurities added in each cycle, it is necessary to discard the residue after hydrolysis, first recovering the sodium carbonate and the iron also if it is found economical to do so.

If dry steam were used for hydrolysis, it would probably be possible to decompose the cyanide without destroying the briquets. It would therefore be possible to return the briquets directly to the furnaces for another nitrification until the carbon content drops too low. Such a large excess of coke is often used in the charge that the composition is not greatly changed in one passage through the furnace, especially if the conversion is comparatively small. Thus, if a conversion of 50 per cent is obtained on a charge containing 25 per cent Na_2CO_3 and 50 per cent carbon, the composition after hydrolysis and reheating would be 26.8 per cent Na_2CO_3, and 46.7 per cent carbon. From these figures it appears that the briquets could be used over at least once if their form were preserved during hydrolysis. A considerable saving could thus be made in the cost of making up the briquets.

h. Separation of sodium cyanide from crude product.—It is as a potential ammonia process that the cyanide process is of greatest interest, but the process might be operated to produce sodium cyanide if desired. Three methods have been considered for obtaining sodium cyanide from the reaction product in which it is mixed with a large proportion of carbon and iron. Bucher originally contemplated leaching it out with water slightly above 35° C. This, of course, would dissolve out the unchanged sodium carbonate as well as the sodium cyanide. It has also been proposed by Bucher and others to distill the cyanide from the reaction product, since sodium cyanide has an appreciable vapor pressure at 1,000° to 1,100° C. This also would fail to give a pure product, as some sodium carbonate would probably distill out as well. The most practicable method at present seems to be the one used in the experimental plant of the Nitrogen Products Co., at Saltville, Va., and in the U. S. C. P. No. 4. In this process sodium cyanide is leached from the cyanized product by liquid anhydrous ammonia, which has a selective solvent action on this compound. The final solution in anhydrous ammonia contains about 8 per cent NaCN. The sodium cyanide is recovered by evaporating the ammonia from the solution. The total time required for the leaching is about three hours. A recovery of 90 per cent of the

NaCN appears practicable. The method has been used only for leaching briquets, and would doubtless be less efficient for a powdered charge since it was found that the presence of fines in the briquets decreased the yield. The ammonia evaporated from the solution is condensed and used repeatedly.

The residue remaining after the leaching out of the sodium cyanide contains sodium carbonate, carbon, and iron, but if a large per cent conversion to sodium cyanide has taken place the constituents are not in suitable proportions to be again treated with nitrogen. It is therefore ground, the proper amounts of coke and soda ash added, and the mixture again made into briquets. The cycle is repeated until the accumulation of impurities necessitates starting with new materials.

i. The Mehner modification of the cyanide process.—A modification of the cyanide process has been experimentally studied by Dr. Herman Mehner in Germany. In this modification the same raw materials are employed as in the usual form of the process, but the method of operation is different. It involves the liberation of the alkali metal from the carbonate by bringing the latter in contact with molten iron containing carbon. The molten iron is circulated by means of a specially designed gas-lift pump. It supplies the heat necessary for the reaction, carries the necessary carbon in solutions, and possibly acts as a catalyst. The volatilized alkali metal is brought into contact with nitrogen and carbon to produce the cyanide. To produce ammonia, the hot cyanide fume is decomposed by water, sodium carbonate being thereby regenerated.

It appears that the process has been carried out only on an experimental scale. Sufficient information with regard to the process and its operation is not available to justify a statement as to its commercial possibilities.

2. Description of Plant.

The only plant of any size which has been constructed for the operation of the cyanide process is the U. S. C. P. No. 4, at Saltsville, Va., built during the war as an emergency measure. For this reason a discussion of the plant required in the cyanide process will have to draw largely on this plant for illustration. Owing to the termination of hostilities about the time of the completion of the Saltville project, the period of operation was too short to point out more than a few of the many changes needed to make the plant smooth running, efficient and well balanced. The description of a cyanide plant will therefore be limited largely to general features, such as the type and capacity of the equipment.

a. Equipment for preparation of charge.—The raw materials must be pulverized and, in the usual modification of the process, formed into briquets suitable for treatment with nitrogen. The first step is the grinding of the coke and iron. Assuming a charge of 30 per cent soda ash, 55 per cent coke, and 15 per cent iron, and assuming 50 per cent conversion to sodium cyanide and 90 per cent conversion of cyanide to ammonia, there is needed about 4 tons of coke and about 1.1 tons of cast iron, or the equivalent of iron oxide, per ton of sodium cyanide, or about 12.8 and 3.45 tons, respectively, per ton of ammonia. A large part of the required coke and iron will, of course, be supplied by disintegrating the briquets coming from the autoclave (or from the leaching system if cyanide is being made). Assuming that a given charge is run through four times before the coke is discarded, and assuming that the iron is recovered from the discarded coke, it is necessary, on the basis of the above assumptions as to charge and yield, to grind about 4.7 tons of coke and about 16.5 tons of returned briquets per ton of ammonia produced.

At the Saltville plant the coke was reduced to the desired size in three operations, a Blake jaw-type crusher, a Sturtevant crusher, and a Patterson ball mill being successively used. The iron dust (bought as such) was introduced in the last stage and ground in the ball mill with the coke, the whole being reduced so that 98 per cent passed through 100 mesh. Sturtevant crushers were used for disintegrating the briquets, but more efficient machinery for this purpose could doubtlessly be obtained, since the briquets are soft. This is a standard grinding problem and need not be dwelt on here.

The required amount of soda ash was added to the iron-coke mixture and the whole charge introduced into a dry mixer. For the assumed charge and yield the dry mixer is required to handle about 23 tons of material per ton of ammonia produced. In using pulverized returned briquets, the coke required to replace that used up is added just before this mixing operation. It is evident, however, that less material will have to be handled provided the yield is greater than the assumed 50 per cent. Many patents claim as high as 90 per cent conversion, although the highest conversion obtained in the Saltville plant over a considerable period was about 50 per cent.

After dry mixing, the charge is wet down with hot water and mixed in a kneading machine until the mass has the consistency of stiff dough. Assuming 20 per cent water, and making the above assumption as to charge and yield, the kneading machine will be required to handle 28 tons of this plastic material per ton of ammonia. The machine is steamjacketed, for it is necessary to keep the mass at nearly 100° C.

The briquetting machine which receives the hot material directly from the kneader contains a plate with holes of the desired diameter through which the plastic charge is extruded in pencils which can be automatically cut to suitable length. The extruder need not be steamjacketed provided it is so designed that the hot material passes through in a short time.

Waste furnace gases are generally available for the driers, which should be placed near the furnaces to utilize the heat effectively. At Saltville the flue gases from the cyanide retort furnaces were used, but considerable difficulty was experienced in getting the necessary temperature because of the distance the hot gases had to travel before entering the driers.

b. Equipment for nitrification.—Metal retorts are used for treating the charge with nitrogen, since no other material has been found suitable as to strength and heat conductivity. The retorts at U. S. C. P. No. 4 were wrought-iron pipes 8 inches by 10 feet 6 inches. Nichrome retorts were also tried. The retorts were placed in an upright position in furnaces fired with producer gas. The actual heating zone inside the furnace was 8 feet 8 inches in length. The retorts were placed in banks of 18, each retort being heated individually.

To minimize the oxidation of the retorts by the flame, the furnaces were provided with two combustion chambers between the gas burners and the retorts, thus obtaining as complete removal of free oxygen from the gases as possible. Iron is not attacked at 1,000° C. by an equilibrium mixture of carbon monoxide, carbon dioxide, and carbon. It was found, however, that, due to the thin walls of the furnaces, it was possible to maintain the temperature required only when combustion was being completed in the retort chamber, and consequently a nonoxidizing atmosphere was not obtained. The exit gases from the furnace contained about 4.5 per cent of free oxygen. That some benefit was derived from the extra combustion chambers in these furnaces is indicated by the fact that the average life of the wrought-iron retorts was about 28 per cent longer than the retorts in the plant of the Nitrogen Products Co., in which the gases traveled over a shorter path before striking the retorts. The average life of the iron retorts was about 300 hours while the nichrome retorts lasted about 1,000 hours.

The producer gas for heating the furnaces was supplied from a Morgan gas-producing machine having a coal-gasifying capacity of 3,000 pounds per hour. The fuel consumption was very greatly in excess of that required to heat the briquetted charge and supply heat for the endothermic reaction. During two observations, for example, about 85 pounds of coal were gasified per "retort hour"; that is, for one hour's heating of one retort. Assuming that a production of about 7 pounds of sodium cyanide per retort hour could be attained in practice, a figure based on the results at Saltville, and assuming a charge of 30 per cent Na_2CO_3, 55 per cent coke, 15 per cent iron, and a 50 per cent conversion, a rough calculation shows that the theoretical coal requirement is about 5 pounds per retort hour. Hence 85 pounds per retort hour corresponds to an efficiency of about 6 per cent. A comparatively low efficiency is, of course, to be expected where it is necessary to heat a solid material of low conductivity indirectly, as in the cyanide process. A higher efficiency than 6 per cent could undoubtedly be obtained with improved design. The low efficiency in these furnaces was due principally to three factors: (1) The furnace walls were not thick enough; (2) the provision of extra combustion chambers to secure the desired long travel of gas before reaching the retorts involved made the furnaces much larger than would otherwise have been necessary, thus providing a very large radiating surface; and (3) the travel of briquets through the retorts was slow.

The feeding arrangement for the retorts at the Saltville plant was typical of the devices which have been suggested and used for this purpose. A screw conveyor supplied the briquets to the top of the retorts, which were provided with a funnel-shaped hopper. At the bottom a gas-tight discharge cock was provided, which opened at intervals and allowed a quantity of the cyanized briquets to fall into a car in which they were cooled in an atmosphere of nitrogen. It was expected that the briquets would move freely down through the retort under the force of gravity, but a great deal of trouble was experienced from the sticking of charges in the retorts, often necessitating the removal of the retorts from the furnace to remove the obstruction. Several workers on the cyanide process have believed that the tendency for the briquets to stick to the walls of the retort would be greatest at the lower end of the retort, where the briquets are cooling and hardening. At the Saltville plant, therefore, the 8-inch pipe was connected to a 9-inch pipe just at the point where the retort went through the floor of the furnace. This enlargement was designed to keep the hot briquets from packing against the walls of the retort until they had cooled below the sticking point. The device, however, did not remedy the difficulty.

The nitrogen required for the treatment of the charge may be obtained by any of the well-known methods. At U. S. C. P. No. 4 it was obtained by the fractionation of liquid air.

c. Equipment for ammonia production.—The production of ammonia from cyanized briquets has never been fully developed on a plant scale, and hence it is possible to consider here only the general type and capacity of the apparatus which would be required. It is evident that the construction of the equipment will depend on whether the hydrolysis is carried out at comparatively high pressure and low temperature (perhaps 300 pounds and 220° C.), or at atmospheric pressure and temperatures up to 650° C. The relative advantages of these two methods have already been discussed in connection with the description of the process. A simple type of autoclave should prove to be satisfactory for the first method. For the second method it is possible that a simple, continuous apparatus could be devised. It would, however, presumably have to be provided with means for external heating.

As to the capacity of hydrolyzing equipment, it has been calculated on the assumptions of (1) a charge containing 30 per cent Na_2CO_3, 15 per cent iron, and 55 per cent coke; (2) a 50 per cent conversion of Na_2CO_3 to NaCN; and (3) a 90 per cent yield of ammonia, that it would be necessary to treat about 22 tons of material per ton of ammonia produced.

d. Equipment for separation of sodium cyanide.—In leaching the briquets at U. S. C. P. No. 4 for sodium cyanide recovery, three closed lixiviators were operated in series on the countercurrent principle. A batch of briquets moved successively from the first to the third, while the fresh anhydrous ammonia was introduced into the third and finally removed from the first, carrying about 8 per cent NaCN. The briquets were leached for about one hour in each lixiviator. The capacity of each lixiviator was 1,000 pounds of briquets per charge. No difficulty was experienced in the leaching operation, provided the briquets did not crumble. The leaching was less efficient when any considerable quantity of fines was introduced.

The ammonia solution of sodium cyanide was drawn off through a stone filter in the bottom of the third lixiviator. The solution was evaporated in a steam-jacketed evaporator provided with a stirrer to prevent caking of the sodium cyanide. The ammonia vapors were superheated somewhat and passed over the drained briquets in the lixiviators in order to evaporate the entrained ammonia. The ammonia was then liquified and stored for further use.

3. Construction and Operating Costs.

It is impossible to give reliable cost figures on the cyanide process, for the reason that the process has never been operated for a sufficiently long time to furnish accurate information.

U. S. C. P. No. 4 was erected as an emergency measure, and the cost of the plant was consequently much higher than in normal times. Its cost was $1,859,346.60, exclusive of barracks and quarters. The plant was designed to yield 10 tons of sodium cyanide per day. From the operation of this plant the conclusion was reached that an output of 7 pounds of sodium cyanide per retort hour could be obtained, and since there were 144 retorts in the plant, the 10-ton output would be obtained with 24 retorts idle, which is probably a sufficient number of spares.

It will be of interest to consider the cost figures obtained at U. S. C. P. No. 4, even though the period of uninterrupted operation was too short to afford accurate cost figures for the process as there developed, and even though the plant was obviously in need of vital modifications which would have affected the costs favorably. A summary of costs based on actual operation is given in the following table:

Summary of costs of the cyanide process.[1]

	Cost per pound NaCN (cents).	Per cent of total cost.
Raw materials	7.4982	37.30
Power	1.5986	7.95
Steam (not used as power)	.3038	1.51
Direct labor	4.5410	22.59
Indirect labor	.4025	2.00
Retort tubes	1.9300	9.60
Repairs	.8220	4.10
Depreciation	1.1800	5.87
Contingencies	1.8260	9.08
Total	20.1021	100.00

[1] Interest and royalties not included.

The cost per pound of sodium cyanide is seen to be $0.201. The corresponding cost of ammonia is $0.53 per pound, assuming all the soda ash returned to the process and the cost of hydrolysis the same as the cost of separation of sodium cyanide. This figure is so high as to discourage any hope that ammonia could be produced economically by any process and plant not differing radically from that at Saltville. The cost of ammonia by the cyanamide process or direct synthetic process is, of course, much lower than the above figure.

Under the heading of raw materials are included several items such as soda ash, liquid ammonia, and containers, which would not be included if the product were ammonia. Moreover, the charge of $0.0234 (per pound of cyanide) for gas coal, which is also included, is extraordinarily high, and it should be possible to greatly lower it in a furnace of better design. This single item of fuel for the producers would amount to about $0.07 per pound of ammonia. The charge for power alone is $0.016 per pound of cyanide, or almost $0.05 per pound of ammonia. Power is required in mixing and making up briquets, in operating the discharge mechanism of the retorts, in operating the blowers to the gas producers, and for general power purposes.

Labor cost is $0.049 per pound of sodium cyanide, or almost $0.15 per pound of ammonia. Labor will probably always be comparatively high in the cyanide process, due to the necessarily small capacity of the units, but it should be possible to cut the above figure very much in a well-designed plant in which the greatest possible use is made of automatic machinery and labor-saving devices.

The figures given in the preceding table were revised by the staff of the plant, assuming normal conditions and a number of modifications of the plant. The total cost, according to this revised estimate, would be $0.09331 per pound of sodium cyanide, not including interest and royalty.

An estimate based largely on the results of the test run in 1918 and observed by representatives of the Nitrate Division at the experimental plant of the Air Reduction Co. indicates a probable cost of about $0.34 per pound of ammonia for a plant having a capacity of 55,000 tons ammonia per year of 350 days.

4. Present Status and Organization of the Industry.

a. *Nitrogen Products Co.*—No plants are known to be in operation at the present time producing either sodium cyanide or ammonia by the Bucher process. The Bucher patents as well as some supplementary patents, such as that of Clancy covering the process of extracting sodium cyanide by liquid anhydrous ammonia, are now owned by the Nitrogen Products Co., of Providence, R. I. So far as is known this company is now doing no work on the process except possibly some experimental investigations at Greene, R. I., the experimental plant at Saltville, Va., having been dismantled.

b. *Air Reduction Co.*—According to a communication from the president of the Air Reduction Co. in November, 1921, no important developments have been made on the process of that company since the test runs in 1918. It is understood, however, that they are continuing their experimental work.

c. *Roessler-Hasslacher Chemical Co.*—The present world supply of pure sodium cyanide is manufactured almost entirely by the Castner-Roessler process, in which metallic sodium, ammonia, and carbon are used. The rights for the use of this process are controlled by the Deutsche Gold und Silber Scheideanstalt, and the process is operated only by licensees of this company. The only manufacturer in the United States using the Castner-Roessler process is the Roessler-Hasslacher Chemical Co., of Perth Amboy, N. J.

d. *The American Cyanamid Co.*—The American Cyanamid Co. has developed a process at their Niagara Falls (Canada) plant for making a crude cyanide by fusing crude calcium cyanamide with sodium chloride. The process is described elsewhere in this report. The product has been used successfully both in metallurgy and in the manufacture of liquid hydrocyanic acid for fumigation.

5. Supply and Demand.

Because of the practice of distributing the available world markets between the different licensees of the Deutsche Gold und Silber Scheideanstalt, the Roessler-Hasslacher Co. has apparently been reluctant to disclose accurate information concerning production or markets in the United States, the statements of different persons connected with the industry being conflicting. Without the cooperation of this company it has been difficult to obtain accurate statistics, since most figures available do not distinguish between sodium cyanide and other compounds of sodium.

a. Production.—From the information available it appears that the production of sodium cyanide in the United States for the years given was approximately as follows:

	Tons.
1914	6,500
1917	8.000
1918	9,000

b. Imports.—The following figures, based on the Statistical Abstract of the United States,[40] show the imports into the United States from 1912 to 1918.

	1912	1913	1914	1915	1916	1917	1918
Total imports of cyanide (calculated as sodium cyanide)........short tons..	1,038	380	306	[1] 3,701	356	334	96

[1] Increased importation from Germany

Although cyanide came from a number of countries, most of it came directly or indirectly from Great Britain and Germany.

c. Consumption.—The largest consumption of cyanide is in metallurgy, being used for the extraction of gold and silver from their ores. Other important uses are in fumigation, particularly of citrus trees, in electroplating, and in casehardening.

Regarding the expected consumption of sodium cyanide in 1918, the Roessler-Hasslacher Co. submitted the following to the War Industries Board:

	Tons.
Metallurgy	3,360
Fumigation of citrus trees	1,400
Other fumigation	196
Electroplating, casehardening, etc	1,400
United States Government contracts	392
French Government contracts	1,344
Total	8,092

An estimate based on figures for partial consumption in 1918 in various industries (not including war contracts) gives the following:

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[40] Published by Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C.

	Tons.
Metallurgy	3,500
Citrus fruit fumigation	1,500
Other fumigation	250
Electroplating, casehardening, and minor uses	500
Total	5,750

The use of hydrocyanic acid for fumigation is comparatively new, and there appears to be a probability of a considerable increase in the demand for cyanides for this purpose. On the other hand, the poisonous character of cyanides will tend to lead to the substitution of other material, if found possible, in electroplating or elsewhere.

d. Present facilities for supplying demand.—The present facilities of the Roessler-Hasslacher Co. are apparently ample to supply any demand for sodium cyanide to be expected in the immediate future, provided a supply of metallic sodium can be obtained. This material is supplied to them by a subsidiary company, the Niagara Electro-Chemical Co. During the war the supply of metallic sodium was interrupted, due to power shortage.

The present capacity of the American Cyanamid Co.'s cyanide plant is not known. An official of the company stated early in 1920,[41] however, that the output for that year would be equivalent to 5,000 tons of sodium cyanide.

6. Future Outlook for the Cyanide Process.

a. For production of sodium cyanide.—A definite statement as to the future possibilities of the cyanide process for the production of sodium cyanide would have to be based in part on accurate cost data on the Castner-Roessler process, the one with which it must compete. Such data are not available, and consequently the general situation only can be stated.

It is believed that the total production cost of sodium cyanide by the Castner-Roessler process is between $0.10 and $0.15 per pound. The actual cost at the U. S. C. P. No. 4, employing the cyanide process, was estimated to be about $0.20 per pound. It has been estimated, however, that under normal conditions and with the improvements in plant operation and design, such as were indicated as being necessary at the U. S. C. P. No. 4, sodium cyanide could be produced at a manufacturing cost of $0.09 to $0.10 per pound, excluding interest, royalties, and sales cost. This estimate assumes the use of a process essentially the same as that employed at the U. S. C. P. No. 4. The process is still in the developmental state, and we may therefore reasonably expect important improvements which will further lower the production cost. On the other hand, since the Castner-Roessler process has undoubtedly reached a high state of development and since the cost of raw materials, ammonia, and metallic sodium will probably continue to be relatively high, no decided reduction in cost by this process is likely.

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[41] Landis. Chem. and Met. Eng., 22 : 265, 1920.

b. For the production of ammonia.—Since the future demand for cyanides, as such, appears to be quite limited, it is only as a potential ammonia process that the cyanide process deserves particular attention. From the fact that the cost of ammonia by this process in its present state will range from two and one-half to three times that of the cyanide, it is quite evident from the preceding discussion that the process now offers no possibilities as compared with established processes for ammonia production. However, since all serious attempts to operate the cyanide process have been limited to essentially the same method of attack, the possibility of a commercially successful production of ammonia from sodium carbonate, carbon, and nitrogen is not absolutely precluded.

The successful development of the cyanide process would require the solution of difficult engineering and chemical problems such as the following: (1) A type of furnace would have to be designed whose heat efficiency is high and in which large charges could be handled and nitrified rapidly without interruption; (2) unusual wear and tear, such as the rapid oxidation of retorts, would have to be avoided in some way; (3) the charge would have to contain a relatively high percentage of sodium carbonate and high conversion would have to be obtained in order that the bulk of materials handled per unit of ammonia should not be excessive; (4) the charge would have to be of such a nature that the nitrogen is absorbed rapidly once the required temperature is reached; (5) the cyanized charge would have to be hydrolyzed in large quantities without the formation of appreciable amounts of ferrocyanide.

Thus, there are undoubtedly many obstacles yet to be overcome before ammonia could be produced economically by the cyanide process. Rapid advances are, however, being made in those branches of engineering which have a bearing on this process; furthermore, it may safely be expected that a much clearer understanding as to the chemical reactions involved will be reached in the near future. In view of these facts, the obstacles can by no means be said to be necessarily insurmountable.

E. OTHER FIXATION PROCESSES.

1. Introduction.

A very large number of methods have been proposed from time to time for the commercial fixation of nitrogen. Excluding the processes to which separate treatment has been given in this report, it must be said that very few of these appear to present promising possibilities at the present time. In many cases no attempt whatever has been made to develop them even on a semicommercial scale, and in other cases where industrial experiments have been made data are not available as to the extent and results of these experiments.

In this section the different processes will be treated in as much detail as their present industrial promise seems to warrant. It must be remembered, however, that unforeseen developments in our knowledge, or changes in the industrial situation due to new demands or supplies, may in the future make possible the commercial success of processes at present entirely impracticable.

2. The Aluminum Nitride (Serpek) Processes.

The different aluminum nitride processes which have been proposed consist essentially in bringing in contact at very high temperature (about 1,800° C.) a mixture of bauxite (crude aluminum oxide), carbon, and nitrogen, when reaction occurs with the formation of aluminum nitride and carbon monoxide, as represented by the equation:

$$Al_2O_3+3C+N_2=Al_2N_2+3CO \qquad (1)$$

It has also been proposed to carry out the reaction in two stages, the first involving the reduction of the alumina (best containing considerable amounts of iron oxide which apparently lowers the temperature of reduction) by carbon at a very high temperature; and the second involving nitrification of the iron-aluminum alloy thus formed at a somewhat lower temperature, the complete reaction being essentially that of equation (1).

In either case the aluminum nitride formed may then be decomposed by steam, dilute acids, or (best) dilute alkalies, with the formation of ammonia and aluminum hydroxide, the reaction being essentially:

$$Al_2N_2+6H_2O=2Al(OH)_3+2NH_3 \qquad (2)$$

The aluminum hydroxide may be reconverted into oxide for repetition of the reaction, but probably it is more economical to use it for the manufacture of metallic aluminum, for which it is well suited.

The temperature of reaction between alumina, carbon, and nitrogen may be lowered somewhat by the presence of other metallic oxides. The absorption of nitrogen begins around 1,100° C., but is rapid only at temperatures near 1,800°. Above 2,200° fusion of the charge practically stops nitrification. The complete reaction (1) occurs with absorption of heat, estimates of the heat of reaction varying between 185,000 calories per mol of nitrogen fixed to 243,000 calories per mol. It is thus necessary, in addition to maintaining the high temperature of reaction, to supply a large amount of heat to the charge. The carbon monoxide evolved during the reaction (1) represents a potential source of heat, as it may be burned with the production of 204,600 calories, making the reaction as a whole exothermic (or slightly endothermic, according to the data used), but from a practical point of view the heat of combustion of the carbon monoxide is by no means equivalent to a corresponding amount of electrical energy. Its use, however, in preheating the charge may effect a considerable economy in the thermal requirements of the process.

Various small-scale experimental plants have been constructed and operated in France, Germany, and the United States. The chief difficulty in all cases is in securing economically the high temperatures necessary for the reaction, and in obtaining materials of construction capable of resisting these temperatures in continuous operation.

A small plant operated in Savoy[42, 43] by the Societe Generale des Nitrures was in operation in 1913, and extensive plans for its expansion were under way, but these plans do not seem to have materialized. The equipment consisted essentially of an inclined rotary, electrically heated kiln, lined with aluminum nitride as refractory. The bauxite, previously preheated by combustion of the hot furnace gases, is mixed with coal and fed from a hopper into the upper end of the kiln, passing through the hot gases into the reaction zone, a section of the kiln fitted with graphite electrodes through which the heating current passes. Here it is raised in temperature to 1,800° and comes in contact with producer gas containing about 75 per cent nitrogen. The time of contact is said to be only a few minutes, and the product, a hard, bluish-gray mass, issues from the lower end of the kiln and is ready for conversion into ammonia and aluminum hydroxide by one of several methods.

The Armour Fertilizer Works had in operation in 1918 an experimental plant at Keokuk, Iowa. This consists essentially of a vertical kiln, about 15 feet high and 4½ feet internal diameter, constricted in the center. At this center constriction a ring electrode of graphite is located, while a pencil electrode of graphite extends down the center of the shaft, its lower end being at the center of the constricted ring. The charge is fed by gravity down the kiln, while the nitrogen (producer gas containing 70 per cent N_2) passes through it in the opposite direction. The charge consists of two kinds of crushed briquets, one of them constituting the reaction mixture proper, and the other aiding in the production of temperature, as indicated below. The reaction briquets are made from crude alumina and coke, with waste sulphite liquor as binder. They are dried and crushed to one-half inch size. The other briquets, which constitute about two-thirds of the total charge, are of carbon and play no part in the reaction, but

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[42] Final report, Nitrogen Products Com., 1910.

[43] Norton: Utilization of Atmospheric Nitrogen, 1912.

carry substantially all the electrical current serving to heat the charge. They can be separated from the product and used again.

When the charge reaches the constriction in the shaft a heavy electrical current is passed through it from the electrodes indicated above, and the temperature is thus maintained at 1,800 to 1,900° C., while producer gas passes through it from below. The rate of feed is so adjusted that the charge is in contact with nitrogen at the temperature of reaction for about one-half hour. At the end of this time about 80 per cent of the theoretical amount of aluminum nitride has been formed. The charge then passes through the lower part of the shaft, being cooled somewhat, and is ready for conversion into ammonia and aluminum hydroxide.

The hot waste gases passing upward serve to preheat the charge, and a portion is recirculated into the lower end of the furnace. This kiln has a capacity of about 400 pounds of nitrogen fixed per day, and requires about 400 kilowatts of electrical energy, or 48,000 kilowatt hours per ton of nitrogen fixed.

It is understood that in 1921 the Armour Fertilizer Works completed a large experimental furnace for the production of fixed nitrogen by this process.

It is also understood that the Aluminum Co. of America has been interested in the aluminum nitride process.

No very reliable data are available as to the cost of plant construction or of operation of plants of either the French or American types.

Estimates, based largely upon theoretical considerations, have been made by Bougeril (Norton, loc. cit.), but it is doubtful if they even represent an approximation.

The Armour Fertilizer Works estimated that their process could operate successfully provided the consumption of electrical energy could be made not over 14,000 kilowatt-hours per ton of nitrogen fixed (compare the 7,000 to 9,000 required theoretically), but it is probable that this can only be achieved in a very large plant.

So far as is known the process is not being operated on a commercial scale at the present time in any country. It possesses, however, sufficient attractiveness to warrant the experimental work which seems to be continually expended upon it. It permits the preparation of a relatively pure aluminum hydroxide from an initially impure product, and this aluminum hydroxide is then excellently adapted for the preparation of metallic aluminum. The ever-increasing demand for this metal suggests that the aluminum nitride process should probably be considered not alone as a nitrogen fixation process but is an aluminum process with ammonia as a by-product. From this standpoint it has greater possibilities, and with mechancial improvements in furnace construction, possible reduction of reaction temperature by catalytic agents and with electrical energy at low cost, it is quite possible that the aluminum nitride process may be economically operated and produce ammonia in competition with other processes.

3. Miscellaneous Metallic Nitride Processes.

In addition to aluminum, many other metals form stable nitrides, and most of these are capable of yielding ammonia or other useful nitrogen compounds after suitable treatment.

Numerous methods have been proposed for nitrogen fixation based upon the general principle of preparing a metallic nitride by treatment of a metal (or a metallic oxide with a reducing agent) with nitrogen gas at more or less elevated temperatures. The metals proposed include magnesium, lithium, titanium, manganese, zinc, boron, and silicon, together with various mixtures.[44] Further treatment of the nitrides is usually proposed—either hydrolysis with steam at high temperature to produce ammonia, or fusion with carbon and alkali carbonate, when cyanides are formed.

So far as is known, none of these ideas has achieved any degree of commercial success, and it does not appear that they have any immediate prospect of such development. Most of them use more expensive materials and are less favorable in results than other well-known processes.

4. Explosion and Combustion Processes.

The explosion (usually called Hausser) process depends for the fixation of nitrogen upon the fact that by exploding a mixture of combustible gas with air or oxygen under proper conditions high enough temperatures can be reached to bring about the combination of a small amount of the nitrogen and oxygen present. As a whole, these processes represent an attempt to bring about the same direct combination of nitrogen and oxygen which occurs in the arc process without the enormous expenditure of electrical energy which the latter process entails. However, reliance upon the energy liberated by the explosion of gases in closed bombs imposes a number of limitations on the process when the much more readily controlled electrical energy is employed.

As the process is essentially a thermal one, the factors determining the formation of nitric oxide are the temperature and the partial pressures of the nitrogen and oxygen in the gases existing at completion of explosion. The total pressure does not influence the percentage conversion except as it may increase the temperature attained. Since the amount of nitric oxide produced from a given amount of combustible gas is the important factor in the cost of the process, it is desirable to consider the influence of the proportions of gas and air in the explosion mixture upon the yield of nitric oxide: (1) The *temperature* will be at a *maximum* when the combustible gas is mixed with the minimum quantity of air necessary to burn it, and will steadily decrease as the mixture is diluted with air. (2) *The product of the partial pressures* of the nitrogen and oxygen after explosion, however, will start to increase as soon as the mixture is diluted with air.

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[44] See Lunge: Ammonia, Vol. III (1916), p. 1095 et seq.

It is evident from the above that dilution with air is disadvantageous to yield as far as its effect on temperature is considered, and advantageous in its effect on the partial pressures of nitrogen and oxygen. It can be readily shown, however, that it is possible to calculate for any given gas the exact mixture which will give the highest possible yield of nitric oxide per unit quantity of combustible gas. If the air is enriched with oxygen the conditions for nitric oxide formation are more favorable, but here also it is possible to determine the optimum conditions.

In case air is used in the explosion, it is evident, since the partial pressures of nitrogen and oxygen must always be less than they are in air alone, that the percentage yield of nitric oxide theoretically obtainable will always be less than that obtained when air alone is heated to the same temperature, as in the electric arc process. This theoretical limit contains only a small percentage of nitric oxide at best.

Use of compressed and preheated gases increases the explosion temperature and, indeed, nearly all small-scale experimental work has been carried out on this plan. The mechanical strains to which the apparatus is subject limit, however, developments along this line.

It appears from the patent literature that Häusser originally contemplated carrying out the process in an explosive engine, the power thus generated being utilized for performing external work. So far as is known, however, all trials have been conducted in stationary bombs with mechanically operated valves. Trial installations have been operated at Heeringen and Neuremberg[45] in which bombs of about 100 liters capacity were employed, the gases being precompressed to 3 to 5 atmospheres and preheated (usually) to 200° to 300° C. The bombs were operated at a speed of 50 explosions per minute, and it was planned to increase this rate somewhat. Coke-oven gas was employed as fuel, and the air was in some cases enriched with oxygen. Analysis of the exhaust gases showed between 0.3 to 0.6 per cent of nitric oxide by volume. The gases passed from the explosion bombs to tubular boilers, the heat absorbed being used partially to preheat the entering gases and partially to generate steam. The recovery of nitric acid was effected by a series of absorption towers similar to those used in the arc process. Concerning costs of construction and operation, two estimates, substantially agreeing, have been made for moderate-sized plants (3,500 metric tons of 94 per cent HNO_3 per year), and are discussed in some detail in the Final Report of the Nitrogen Products Committee. These estimates assume the use of low-priced coke-oven gas, and no use of the power produced by the explosion, though the steam power of the hot gases is allowed for. Both estimates give a cost of nitric acid of the same order as that involved in its production from Chile sodium nitrate.

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[45] Final report Nitrogen Products Com. (1920).

It is, however, gravely doubtful whether the process as at present developed has a chance of competing successfully with other nitrogen fixation processes. There are two possible ways in which marked improvement might be made. If a gas engine could be developed which could operate successfully under the conditions of the process and utilize the explosive pressure for power production, then the process might be capable of being installed for power production, with nitric acid as a by-product, and might prove highly successful. A second possibility is some marked improvement in our ability to absorb dilute nitric oxide. With our present methods the enormous towers necessary for the absorption of the dilute nitric oxide produced by this process militate strongly against its ultimate adoption. It must be regarded, however, as having distinct possibilities of commercial success.

Closely related to the Häusser process are a number of attempts to effect the combination of nitrogen and oxygen by burning a mixture of air with some combustible gas and thus producing a very high temperature. Most of the proposed schemes hinge upon the method of producing the high temperature. The method proposed by Bender seems to have attracted greatest attention. His plan is to use either an ordinary furnace or a gas producer admitting compressed air (enriched with oxygen) immediately above the fuel bed in order to produce a very high temperature. Into the hottest zone he injects steam, which is said to dissociate partially into hydrogen and oxygen, which then recombine in the cooler part of the furnace, producing an extremely hot flame which brings about the combination of the nitrogen and oxygen. (It may be noted that the dissociation of water into hydrogen and oxygen is only 4 per cent at atmospheric pressure at 2,500° C., and that in any case the recombination can hardly give rise to a hotter flame than that causing the dissociation.)

Others have suggested combustion of carbon monoxide or water gas under high pressure as a means of attaining the desired high temperatures.

In any case the burned gases are to be cooled as rapidly as possible, usually by a boiler arrangement, and the nitric oxide absorbed as in the case of the Häusser gases.

Numerous theoretical objections present themselves in considering such processes. Where it is conceivable that by proper regenerative heating of the gases before combustion, and by burning them under pressure, temperatures equal to those of the Häusser process might be obtained, it is difficult to conceive of an effective mechanism for cooling these gases sufficiently rapidly to prevent the breaking up of the nitric oxide. Furthermore, materials capable of withstanding continuously the temperatures in question represent a difficult problem.

Altogether there seems no reason to believe that any of the combustion processes as at present proposed give any promise of commercial success.

5. Miscellaneous Metallic Cyanide Processes.

Excluding the sodium cyanide process, to which a separate section of this chapter is devoted, a number of other cyanide processes for nitrogen fixation deserve some attention.

The fixation of nitrogen as barium cyanide is perhaps the best known of these processes, and the one which has been operated on the largest scale. The process may be carried out either in a single stage or in two stages. In the single-stage process a mixture of barium carbonate (or oxide) and carbon (usually briquetted with tar or pitch) is heated to a temperature of 1,000° to 1,400° C., while nitrogen gas is passed over it. Under these conditions the final reaction is:

$$BaCO_3+2C+N_2=Ba(CN)_2+CO_2 \qquad (3)$$

In the two-stage process barium carbide is first formed by treatment of barium oxide and carbon in an electric furnace:

$$BaO+3C=BaC_2+CO \qquad (4)$$

The barium carbide is then treated with nitrogen gas at about 1,000° C., when barium cyanide is formed, probably with the intermediate formation of barium cyanamide:

$$BaC_2+N_2=BaCN_2+C \qquad (5)$$

$$BaCN_2+C=Ba(CN)_2 \qquad (6)$$

Numerous minor variations from the above essential ideas are expressed in the patent literature.

In any case the barium cyanide formed is treated with steam, when hydrolysis into ammonia and barium hydroxide occurs, in accordance with the following reaction:

$$Ba(CN_2+4H_2O=2NH_3+Ba(OH)_2+2CO \qquad (7)$$

The resulting barium hydroxide may be used over again to regenerate the cyanide.

The two-stage process resembles closely the manufacture of cyanamide, while the single-stage process resembles somewhat the manufacture of sodium cyanide.

As compared with the cyanamide process, there is the obvious disadvantage in that barium carbonate is much more expensive than calcium carbonate, and that furthermore the final product must be converted into ammonia, whereas cyanamide is capable of direct utilization for fertilizing purposes. The economical recovery of the barium hydroxide also presents some difficulties.

As compared with the sodium cyanide process, almost the same arguments hold.

Altogether there seems no reason to believe that the barium cyanide process is as satisfactory as either of the above-mentioned methods. It has never been developed on a commercial scale and is apparently not being considered seriously at the present time.

It may be noted that in 1843 a plant was established in Paris for the production of potassium ferrocyanide through potassium cyanide from atmospheric nitrogen. Coke, impregnated with potassium carbonate, was heated to a high temperature in an atmosphere of nitrogen. The plant was designed to produce potassium ferrocyanide and had a capacity of a ton a day. It was, however, abandoned in 1847 as too costly. Similar experiments were carried out on potassium cyanide formation by Newton in England in 1843, but were abandoned after a short time.

In 1907 the Badische Co. brought forward a method for nitrogen fixation based upon the formation of titanium cyanide (mixed with nitride) when titanium oxide is heated with carbon in a current of nitrogen. This material, said to have the formula $Ti_{10}C_2N_8$, may be heated with carbon and sodium carbonate, or with barium or calcium carbonate, when titanium oxide is re-generated and alkaline or alkaline earth cyanides and cyanamides are formed. An alternative method of treatment consists in boiling the titanium compound with sulphuric acid, when the nitrogen is converted into ammonium sulphate and the titanium reconverted into oxide. So far no commercial developments of the process have appeared.

Compounds of the same general type, sometimes called carbonitrides, of aluminum and other metals, have been proposed in connection with nitrogen fixation, but none of them seem at present to offer attractive possibilities.

6. Hydrocyanic Acid Processes.

Several processes have been proposed for the direct production of hydrocyanic acid from mixtures of hydrocarbons and nitrogen. Thus

Berthelot showed as early as 1869 that acetylene and nitrogen coming under the influence of a silent electric discharge tend to form hydrocyanic acid, according to the equation:

$$C_2H_2+N_2=2HCN.$$

Later Hoyermann employed the electric arc to bring about the reaction. A recent process of the Chemischerfabrik Griesheim Elektron passes nitrogen and hydrogen over coke in an electric furnace where formation of hydrocyanic acid is said to occur. A French company has proposed a similar process. Lipinsky has proposed passing electric discharges through a mixture of methane (from natural gas), nitrogen, and hydrogen, when combination to form ammonia and hydrocyanic acid is said to occur.

In all of these processes the hydrocyanic acid is either absorbed by alkalies to form cyanides, burned with air to form nitric oxide (for final conversion into nitric acid), or hydrolyzed with steam at high temperatures into ammonia.

Apparently none of these ideas have met with any degree of commercial development, and it can not be said that they have material promise in the present state of our knowledge.

CHAPTER V.

NITROGEN CONVERSION PROCESSES.

A. AMMONIA OXIDATION.

1. History and Present Status of the Industry.

The relation between nitrate nitrogen and ammonia nitrogen in the world supply has been discussed in Chapter II. For use in agriculture the two forms of nitrogen are interchangeable to a great extent, but for most other purposes either one form or the other is required. The domestic supply of inorganic nitrogen in all the great manufacturing countries is mainly in the form of ammonia, while the imports of nitrogen consist mainly of nitrate of soda from Chile. The two leading nitrogen fixation processes—the cyanamide process and the direct synthetic or Haber process—yield ammonia as their product, and the nitrogen recovered from coal distillation is in the form of ammonia. Ordinarily the interchangeability of these compounds for use in agriculture has given the supply enough elasticity to cover all demands and has caused the price of nitrate and ammonia compounds to be nearly the same per unit of nitrogen. Scientists have long been aware of the fact that conditions might arise which would make desirable the conversion of ammonia into nitrate, and their expectations were fully realized during the World War.

Many methods for oxidizing ammonia were worked out on a laboratory scale during the last century. The use of nitrifying bacteria, always present in the soil, for the conversion of organic ammoniates into saltpeter is almost as old as the use of gunpowder and was used extensively on the saltpeter plantations of northern Europe 200 years ago. Some rather promising progress has been made during the last 20 years in the use of bacteria for the oxidation of inorganic ammonia, but this method has not been used on an industrial scale. The present industrial methods for ammonia oxidation come from a series of experiments in which ammonia gas-air mixtures or ammonia gas-oxygen mixtures of varying concentrations were passed over a heated catalyst. Finely divided nickel, finely divided copper, lead manganate, lead permanganate or bichromate, alkaline earth plumbates, the higher oxides of manganese, lead, copper, silver, iron, cobalt, and nickel, platinized asbestos, and platinum wire or foil are some of the materials which have been used as catalyzers.

The fundamental principles underlying the ammonia oxidation reaction were established by the German chemist, Ostwald, after a series of studies beginning over 25 years ago. He took up the study in his usual scientific manner and established the essential facts upon which the design of all the industrial installations have been based. He determined the most suitable ammonia-air mixture for efficient oxidation, and demonstrated that for such a mixture a supply of heat above that directly generated by the reaction was necessary for the most efficient oxidation. He noted the activation of dense platinum when operated under proper conditions and demonstrated the advantages of dense platinum over other forms of catalyst. He showed that platinum black is entirely unsuitable as a catalyst because of the difficulty of removing the products promptly from contact with the catalyst. The Ostwald converter consisted of two concentric tubes, with the catalyzer built up of narrow strips of platinum foil in the end of the inner tube. The exterior tube was of heat-resisting and heat-insulating material; the inner tube was of nickel. The ammonia-air mixture entered the exterior tube at one end, passed along the annular space in contact with the hot inner tube, then through the catalyzer in the end of the nickel tube and out through the nickel tube, which acted as a heat interchanger to preheat the incoming ammonia-air mixture and cool the products of the reaction. The ammonia-air mixture was prepared by blowing air through aqua ammonia. This apparatus as built by Ostwald was theoretically sound and lacked only the use of platinum gauze to have all the essential features of the most improved apparatus of the present time.

Another German chemist, Kaiser, carried on extensive investigations on the oxidation of ammonia. He used a platinum gauze catalyst and preheated the air before adding the ammonia. He also tried activating the air by silent discharge, and in these experiments reported conversion efficiency above 100 per cent, results which were doubtless due to errors in the method of analysis used.

The first plant for using the Ostwald process on an industrial scale was built at Gerte, in Westphalia, in 1909. The details of the process had been carefully worked out before attempting its use on an industrial scale, as is shown by the fact that this plant operated very successfully in the manufacture of ammonium nitrate. The process was later purchased by the Nitrate Products Co. (Ltd.), of London, and this company continued the operation of the factory in Westphalia and built a second factory in Belgium in 1911.

The World War brought about conditions, for the first time, which demanded the conversion of great quantities of ammonia into nitric acid, and oxidation plants of great capacity were built to fill the war emergency. The major part of Germany's supply of nitric acid was manufactured by this process after the first year of the war. France built six oxidation plants, and in the United States two large plants were built by the Government and others of small capacity by private enterprise. Italy, England, and other countries have oxidation plants also.

Table I gives some interesting data on four of the largest oxidation plants. From this table it will be seen that the total annual capacity of these four plants in nitrate nitrogen produced is about 100,000 tons, or as 100 per cent nitric acid about 450,000 tons.

TABLE I.—*Typical ammonia oxidation plants.*

Plant.	Location.	Source of ammonia employed.	Catalyst employed.	Annual capacity.	Approximate production.	
					Tons of product.	Tons of nitrogen.
1	Germany	Synthetic ammonium sulphate and gas liquor.	Activated iron oxide.	35,000 tons nitrogen.	80,000 tons nitrate of soda and 15,000 tons nitric acid (as 100 per cent).	16,000
2	...do.....	Gas liquor ammonia liquor from cyanamide and synthetic ammonia.	Platinum gauze without electric heating.	18,000 tons nitrogen.	60,000 tons nitric acid.	13,000
3	United States.	Ammonia from cyanamide.	Platinum gauze with electric heating.	110,000 tons of ammonium nitrate.	(1)..............	(1)
4	...do.....	Synthetic ammonia and aqua ammonia.	Platinum gauze without electric heating.	22,000 tons of ammonium nitrate.	(1)..............	(1)

[1] Used only for test operations.

With the signing of the armistice the conditions which had stimulated the development of ammonia oxidation since 1914 came to an end. The process had been used extensively for making 50 per cent nitric acid to be used in various ways in the manufacture of munitions, and to a less extent in the production of sodium nitrite for the dye industry, and in the production of nitrogen oxides for the chamber sulphuric acid plants to take the place of sodium nitrate which is usually used in the chamber process. Since the armistice the feasibility of using the oxidation plants for converting ammonia into ammonium nitrate for use in agriculture has been given serious consideration, but material progress has been made only in Germany in connection with the direct synthetic fixation plants where conditions are unusually favorable since these plants produce great quantities of ammonia for conversion into some salt suitable for use in agriculture.

2. Description of the Process.

The fundamental principles involved in the production of nitric acid from ammonia are expressed in the following reactions:

$$4NH_3+5O_2=4NO+6H_2O \qquad (1)$$

$$2NO+O_2=2NO_2 \qquad (2)$$

$$3NO_2+H_2O=2HNO_3+NO \qquad (3)$$

A reoxidation of NO and a duplication of reactions (2) and (3) (4)

The reaction (1) takes place only at high temperatures (around 700° to 1,000° C.) and in the presence of a catalyst. Platinum gauze has been used exclusively as the catalyst in the United States, although a large number of materials have been suggested and very good results have been obtained with some of them. In the United States only ammonia-air mixtures have been used, in which case reaction (1) becomes

$$4NH_3+5O_2+18.8N_2+Pt=4NO+18.8N_2+6H_2O+Pt+211{,}750\text{ g. cals.} \qquad (5)$$

In the case of a 10 per cent NH_3 gas mixture, we have

$$10NH_3+2.8H_2O+18.3O_2+68.9N_2=10NO+17.8H_2O+68.9N_2+5.8O_2 \qquad (6)$$

Or in the case of a 12 per cent mixture.

$$12NH_3+2.8H_2O+17.9O_2+67.3N_2=12NO+20.8H_2O+67.3N_2+2.9O_2 \qquad (7)$$

Or in the case of a 14 per cent mixture

$$14NH_3+2.8H_2O+17.5O_2+65.7N_2=14NO+23.8H_2O+65.7N_2+(O_2\text{none}) \qquad (8)$$

From these equations it will be seen that a 14 per cent NH_3 mixture carrying 2.8 per cent water vapor has just enough oxygen to satisfy the equation, with no excess oxygen in the product of this reaction. The 12 per cent mixture will have 2.8 per cent excess oxygen and the 10 per cent mixture 5.6 per cent excess oxygen.

From a study of reactions (2) and (3) it will be seen that the excess oxygen in the products of reaction (1), in the case of a 10 per cent NH_3 mixture, is not sufficient to complete the oxidation to nitric acid. In actual operation this is not a serious objection to using mixtures high in ammonia, for the requisite amount of air is easily admitted during the cooling and absorption stages of the process. However, for other reasons it is advantageous to have a rather large excess of oxygen passing through the catalyzer. In addition to reaction (1), in which the nitrogen of the ammonia is oxidized to an oxide of nitrogen, other reactions, such as (9) and (10), occur in the catalyzer and cause the loss of fixed nitrogen.

$$4NH_3+5O_2=4NO+6H_2O \qquad (1)$$

$$4NH_3+3O_2=2N_2+6H_2O \qquad (9)$$

$$4NH_3+6NO=5N_2+6H_2O \qquad (10)$$

Reactions (9) and (10) require less oxygen than reaction (1), and their occurrence is promoted by low oxygen concentration. Experience in the operation of ammonia-nitric acid converters has confirmed what a study of the reactions would indicate, i. e., that the highest percentage of conversion can be obtained only when the ammonia concentration is kept below 10 per cent.

The relation of the ammonia concentration in the gas mixture to efficiency of conversion is somewhat complicated if the heat of the reaction is relied upon entirely to keep up the temperature of the catalyst. As indicated in equation (5), a very large amount of heat is generated by the reaction. In a properly constructed converter, using platinum gauze, the heat generated by even a 9 per cent NH_3 mixture is sufficient to sustain the reaction. However, even in a converter so well built as to prevent all unnecessary losses of heat, the heat generated by the reaction is not sufficient to maintain the catalyst at the high temperature required for the best results. In such a case the temperature conditions become better as the amount of ammonia in the mixture is increased from 9.5 per cent to 12.5 per cent, so that the beneficial effects of higher temperatures balance the harmful effect of low oxygen, with the result that efficiency of conversion is not materially altered by changes of ammonia concentration within these limits. However, this does not hold true when some means is provided for maintaining a constant higher gauze temperature—as by electrical heating or by preheating the air for the ammonia-air mixture—in which case the advantages of mixture low in ammonia and correspondingly high in oxygen have been proven. The reaction on the gauze is started by merely heating the gauze, or a part of the gauze, to a red heat while passing the ammonia-air mixture through it. In the electrically heated converter this is accomplished by the use of electricity, while in the nonheated type it is done by applying a torch to the gauze.

Ammonia-air mixtures carrying 10 to 12 per cent are nonexplosive at ordinary temperatures, but when subjected to a red heat burn to nitrogen and water, according to the reaction

$$4NH_3+3O_2=2N_2+6H_2O. \qquad (9)$$

Ammonia-air mixtures become explosive as the ammonia content approaches the theoretical amount required to completely burn the oxygen in the air, as shown in equation (9). In ammonia-air mixtures of all proportions the ammonia is decomposed if brought in contact with most materials at dull red heat. Nickel, aluminum, and silica are exceptional in that they can be used in contact with hot ammonia-air mixtures.

To obtain the second reaction in the oxidation process as shown by the equation

$$2NO+O_2=2NO_2 \qquad (2)$$

it is necessary to cool the hot gases coming from the catalyst as has been shown in section 2–b "Oxidation of nitric oxide" of the arc process. This reaction proceeds rather slowly, making it necessary to allow considerable space to hold the gases while this reaction goes to completion. Attempts have been made to use a catalyst to speed up reaction (2) and this phase of the process is an important one from the standpoint of economy in tower construction. The most successful attempt to catalyze the oxidation of nitric oxide to nitrogen dioxide is that accomplished by the use of a special charcoal, particularly such charcoal as was developed for use in the American gas masks. However, this material has the serious fault of catching fire when used in a rich nitrous gas mixture.

The last step in the formation of nitric acid takes place when the gas is brought in contact with water as expressed in the equation

$$3NO_2+H_2O=2HNO_3+NO \qquad (3)$$

By circulating the gas and the liquid in such a way that the rich gas, coming direct from the coolers, comes in contact with the nitric acid solution of highest concentration, a product can be made containing 50 per cent nitric acid, or under favorable conditions as high as 55 per cent nitric acid. The rate of absorption falls off rapidly after the concentration of the acid reaches 45 per cent and stops entirely at 50 or 55 per cent, depending upon temperature conditions and upon the concentration of the gas, low temperatures and high gas concentration being favorable for the production of strong nitric acid.

3. Comparison of Oxidation Plants at Nitrate Plants Nos. 1 and 2.

A description of the ammonia oxidation equipment at United States Nitrate Plant No. 1 and at United States Nitrate Plant No. 2 will be found in Appendices A and B, respectively.

The two plants differ in the following items: Plant No. 1 is equipped for using liquid ammonia from the direct synthetic ammonia plant or aqua ammonia from the by-product coke ovens, while plant No. 2 is equipped for using ammonia gas from the cyanamide autoclaves. The catalyzers at plant No. 2 use a single, flat gauze electrically heated, while those at plant No. 1 are of cylindrical, multiple layer gauze type with no provision for heating the gauze or for preheating the ammonia-air mixture. The high temperature coolers at plant No. 1 are simply 12-inch cast-iron pipes exposed to the air, while at plant No. 2 the hot gas is cooled in low-pressure boilers. The low temperature coolers and absorption towers at the two plants are identical. The acid lifts for circulating the dilute acid over the absorption towers differ in type at the two plants. The following table shows the essential characteristics of the two systems of lifts:

	Plant No. 1.	Plant No. 2.
Pipe material	Duriron.	Aluminum.
Weight per foot of pipe . . . pounds	15	3
Number of lifts in series	2	1
Inside diameter of pipe . . . inches	3	2¼
Total length of vertical pipe including vent from first lift . . . feet	258	273
Submersion . . . per cent	50	58
Acid delivered per minute . . . gallons	45	60
Air required per gallon of acid delivered (measured as free air) . . . cubic feet	3	1.3
Air pressure in manifold supplying lifts . . . pounds	30	70
Air pressure in pipe leading to first lift . . . do	13	50
Air pressure in pipe leading to second lift . . . do	25	....
Net height to which acid is pumped . . . feet	73	73

The cylindrical type catalyzer used at plant No. 1 has the advantage of low first cost and requires no electrical energy. On the other hand, it has not proven successful for operation on cyanamide ammonia, due to certain catalytic poisons occurring in the cyanamide ammonia. The electrically heated catalyzer as used at plant No. 2 has good temperature control, which enables it to work successfully on impure ammonia gas. It is also possible to maintain the gauze temperature while using ammonia-air mixtures low in ammonia, and for this reason has given better conversion efficiency when used on a large scale. The characteristics of the two catalyzers are shown in the table which follows:

Comparison of catalyzers at plants Nos. 1 and 2.

	Flat electrically heated, Plant No. 2.	Cylindrical multilayer, Plant No. 1.
Dimension of exposed layer	12 by 24 inches	11.5 by 9 inches diameter.
Size of gauze	13 by 27 inches	13 by 114 inches.
Number of layers	1	4.
Shape	Flat rectangular	Cylindrical.
Size of wire in gauze	0.0030 inch	0.0026 inch.
Mesh per lineal inch, gauze	80	80.
Total weight of platinum	5.20 ounces	16.50 ounces.
Total cubic feet gas per minute	42	190.
Cubic feet gas per minute per square foot, gauze	21	21.

4. Construction and Operating Costs.

The ammonia oxidation plant at United States Nitrate Plant No. 2 cost approximately $13,000,000. Since this plant was built during the war, when construction costs were very high, it is believed that

60 per cent of the above cost, or $7,800,000, represents more nearly the normal cost of such a plant. The annual capacity of the plant is 190,000 tons of 50 per cent nitric acid, or 95,000 tons figured on the 100 per cent HNO_3 basis. Then, the construction cost per annual ton of 100 per cent nitric acid is $82. The cost of nitric acid by the ammonia oxidation process should include interest, depreciation, obsolescence, insurance, and taxes at 15 per cent of $82, or $12.30 per ton of 100 per cent HNO_3.

Allowance should also be made for the interest on working capital. Appendix C of this report contains the estimated cost of producing nitric acid at plant No. 2, but does not include the item mentioned above for interest, depreciation, obsolescence, insurance, and taxes, or the interest on working capital.

If the unit cost of ammonia is taken as $211.30 per ton, as shown in Chapter IV, cyanamide process, of this report, and other items are taken as shown in Appendix C, the cost of nitric acid will be as shown below:

Ammonia gas (0.317 tons, at $211.30)	$66.98
Power (4 mills per kw. hr.), compressed air, miscellaneous supplies, and repair parts, labor, and superintendence	7.36
Interest, depreciation, obsolescence, insurance, and taxes, at 15 per cent of $82	12.30
Total per ton, 100 per cent HNO_3	86.64

No allowance for royalties has been made in this estimate.

B. AMMONIUM SULPHATE.

1. Introduction.

The manufacture of ammonium sulphate has now become a very important industry, due to the rapidly growing demand for the material as a fertilizer. The world's production of ammonium sulphate for 1918, for example, was approximately 2,000,000 tons.

The principal method of making ammonium sulphate consists in passing ammonia gas into sulphuric acid. The product is a crystalline compound containing from 20 to 21 per cent nitrogen, white when pure. The fertilizer grades are frequently grayish white or brown, due to impurities.

a. Sources of ammonia.—The sources of ammonia may be grouped under two general heads—by-product and synthetic. The former source is by far the more important at the present time in practically all of the countries except Germany and, possibly, Scandinavia. Ammonia is obtained as a by-product mainly in the destructive distillation of bituminous coal for the manufacture of coke and gas. By-product sources of lesser importance are peat, shale, refuse animal products, and sewage. Synthetic ammonia is obtained almost entirely from the Haber and cyanamide processes of nitrogen fixation.

b. Sources of sulphuric acid and substitutes.—For the production of sulphuric acid, brimstone is burned, or sulphides of iron, copper, zinc, etc., are roasted to produce sulphur-dioxide fumes, which are then oxidized and converted into the acid by either of the two well-known processes, namely, the chamber and contact processes. The former furnishes about 90 per cent of the total acid produced, the latter being used mainly for making concentrated acid. The chamber process produces an acid of a concentration (50° to 60° Bé.) suitable for direct use in ammonium sulphate manufacture.

Since it requires about 3.72 tons of 60° B. sulphuric acid to fix 1 ton of ammonia as sulphate, it is seen that the cost of acid is an important item in the total cost of the sulphate. Numerous attempts have therefore been made to manufacture ammonium sulphate without the use of the acid. Among the more important may be mentioned the absorption of ammonia in niter cake; its absorption in superphosphate; the utilization of sulphur compounds in coal, at coke and gas works, for the formation of sulphate; and the decomposition of gypsum in water suspension by the simultaneous treatment with ammonia and carbon dioxide. None of these processes has become commercially important except the last, and that only in Germany. It is possible, however, that some of the others may eventually be developed to operate successfully in cases of certain combinations of chemical manufacturing processes.

2. Description of Processes.

The principal difference between by-product and synthetic ammonia gas from the standpoint of sulphate manufacture is in the concentration. Coke-oven gas, for example, generally contains only 1 to 2 per cent of ammonia, while synthetic gas is practically 100 per cent ammonia. In the older, indirect processes of by-product ammonia recovery, however, a more concentrated gas was produced by distilling ammonia liquor. Differences in gas concentration necessitates somewhat different methods of absorption, as is pointed out in the following sections.

a. Process using dilute gas.—Since the manufacture of ammonium sulphate, particularly from by-product ammonia, has been so fully described by Lunge[1] and others, it will be but briefly outlined in this report for purposes of comparison with the less known process for concentrated ammonia gas.

In the older processes sulphuric acid was first neutralized with ammonia gas and the resulting solution then evaporated in a separate vessel to obtain the ammonium sulphate. It was soon found, however, that by proper selection of acid and gas concentration and feed that the process could be carried out continuously by utilizing the heat evolved on absorption of gas in the acid to concentrate the solution in the absorber itself. The sulphate crystals continuously separate from the hot, saturated solution and are removed from the bottom of the absorber without interrupting the neutralizing operation.

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[1] Coal Tar and Ammonia. Part III, Ammonia. D. Van Nostrand, New York, 1916.

In the case of dilute ammonia gas, 1 to 2 per cent ammonia, such as from coke ovens, the process consists in passing the preheated and tar-free gas into 50° to 60° Be. (62 to 78 per cent) acid. In normal operation the temperature of the solution is maintained at about 135° F. by regulating the gas and acid feed. Although the solution is far below the boiling point, the water is continuously carried off by the large volume of gas accompanying the ammonia. The heat of evaporation is supplied by the heat of neutralization. An acid trap is used to recover any acid carried off as a mist. The sulphate crystals are removed from the absorber bottom by steam or air lifts to drain boxes where the accompanying mother liquor drains off and returns to the absorber. The crystals are centrifuged to further dry them, and if a dry product is required they are passed through a rotary drier.

b. Process using concentrated gas.—The process using concentrated gas differs from that for dilute gas principally in the temperature of operation and in the concentration of acid in the absorber. The practically pure ammonia gas is passed into acid containing about 7 per cent H_2SO_4. The heat of neutralization maintains the solution at 212° to 215° F., so that water passes off in the form of steam. To recover any unabsorbed ammonia, the vapors leaving the absorber are passed up through an acid "scrubbing tower." The tower also serves to prevent loss of acid in the form of mist. The initial concentration of acid in this process is practically the same as for the dilute gas process, but after passing down through the "scrubbing tower" and after being diluted by wash water from the centrifugals it contains approximately 7 per cent H_2SO_4. The removal and treatment of the crystals is essentially the same as in the other process.

The high-temperature absorption introduces a number of operating difficulties not encountered at the lower temperature. The grain size is smaller, making the salt more difficult to dry in the centrifugals; an interruption in operation quickly leads to "salting up" of pipes and troughs due to the high concentration of salt in the mother liquor; steam given off from troughs, drain boxes, etc., is objectionable to operators; and the life of the lead lining in absorber, troughs, and boxes is considerably shortened. On the other hand, the additional equipment required to handle the large volume of gas in the dilute gas process materially increases the equipment and operating costs of the plant.

c. Gypsum process.—The use of gypsum and carbon dioxide as a substitute for sulphuric acid in the manufacture of ammonium sulphate has been already referred to. This process as operated in Germany[2] consists in subjecting a paste of finely ground gypsum and water to the action of ammonia and carbon dioxide, the reaction being essentially as represented by the equation

$$Ca\ SO_4+H_2O+2NH_3+CO_2=(NH_4)_2SO_4+CaCO_3.$$

The duration of the reaction is said to be from 9 to 10 hours. The carbonate is filtered off and the ammonium sulphate is obtained from the filtrate, which contains about 25 per cent $(NH_4)_2SO_4$, by concentration and centrifugation. The plant at Oppau, Germany, has a capacity for treating 1,000 tons of gypsum per day, corresponding to 925 tons of ammonium sulphate.

This process is particularly applicable in localities where gypsum may be obtained very cheaply for operation in conjunction with the Haber-Bosch process, which produces an available supply of by-product carbon dioxide.

3. Plant Equipment.

The manufacture of ammonium sulphate using concentrated ammonia gas, as from the cyanamide or Haber processes, for example, requires plant equipment of somewhat different design than when using a dilute gas such as that from coke ovens. In this connection it may be mentioned that attempts in Germany to use a by-product ammonium sulphate plant for concentrated gas (synthetic) are understood to have failed.

By-product ammonium sulphate equipment has been described by Lunge (previously quoted) and others and therefore need not be considered in this report. A recent modification,[3] however, will be mentioned. The gas from the coke ovens is cooled, passed through a tar extractor, and the moist gases introduced into two adjacent compartments of a three-compartment absorber. The ammonia is absorbed by the acid, and the other gases are then preheated and passed into the third compartment, where the necessary evaporation is effected.

Equipment for the manufacture of ammonium sulphate from concentrated ammonia differs so greatly from the by-product equipment that a brief general description, based mainly on the proposed ammonium sulphate installation at the Muscle Shoals plant, will be given.

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[2] Chem. and Met. Eng., 24 : 391 (1921).

[3] U. S. patent 1366111 (1921).

The following description applies to a plant unit having an estimated capacity of 60 tons of ammonium sulphate per 24 hours. The saturator or absorber consists of a lead-lined tank having a lead-lined cast-iron cover. To assist in obtaining a satisfactory distribution of ammonia in the solution it is preferable to have the length of the tank about three times the width and the depth approximately the same as the width. To facilitate the removal of the crystals the lower half of the side and end walls are tapered inward. The saturator for a 60-ton unit should have a capacity of about 10,000 gallons. The saturator may be constructed of wood or iron, heavy sheet lead being used for lining in either case. It is desirable to have an emergency tank directly beneath the saturator in case the latter has to be drained quickly.

The ammonia gas is introduced into the 7 per cent sulphuric acid solution by means of three distributors equally spaced lengthwise of the tank, and which pass through the cover to within about 2 feet of the bottom. Four duriron ejectors, actuated by steam jets introduced through the floor, are placed in line with ammonia inlet pipes and serve to remove the crystals from the bottom of the saturator to a distributing trough connected with three drain boxes. The trough and drain boxes may also be constructed of wood and the lead lining protected by acid-proof tile.

The drained crystals are further freed from the mother liquor in centrifuges in which they may also be washed with hot water. About eight 40-inch centrifugal driers are required for a 60-ton unit. To reduce the moisture content below 4 to 5 per cent a rotary steam-heated air drier may be advantageously used.

An acid-absorption tower is provided to recover any unabsorbed ammonia escaping from the saturator. The tower is constructed of acid-proof brick and packed with tile in such a manner that ammonia entering the bottom is completely absorbed by the acid trickling over the packing. The acid is fed from the supply tank through a flow gauge into an acid-distributing box at the top of the tower. The supply tank may be constructed either of steel or of wood (lead lined), since 60° Bé. acid is used in the process.

A steam hood extending over the absorber, drain boxes, and centrifuges is provided to continuously remove the steam from the building.

4. Present Status of Ammonium Sulphate Industry.

The various sources of ammonia have been previously mentioned. At the present time ammonia is being produced on a commercial scale in this country only as a by-product in the manufacture of coke, gas, and bone black, and of these three sources by-product coke plants produce most of the sulphate. In 1919 about 89 per cent was obtained from this source.[4]

Ammonium sulphate has been produced from cyanamide to a very limited extent in this country by the American Cyanamid Co. It is understood that the plant is not in operation at the present time.

The domestic production of ammonium sulphate has increased rapidly during the years 1913 to 1919 as shown by Table 10, Chapter II.

The production of synthetic ammonia will introduce a new factor into the ammonium sulphate industry. At the present time, however, the quantity so produced is not of sufficient importance to noticeably affect the industry except in Germany.

5. Demand for Product and Future Outlook.

The demand for combined nitrogen for fertilizer purposes is increasing rapidly. The use of ammonium sulphate as a fertilizer material grew very rapidly before the war and during the war its use was still further extended, due to the diverting of Chilean nitrate from agricultural to munition purposes. As a result, ammonium sulphate has now become one of the principal nitrogenous fertilizer materials.

Coal, peat, and similar material represent enormous reserves of ammonia nitrogen. The various grades of coal differ quite markedly in nitrogen content, but on the average contain about 1.25 per cent. Although only about 20 per cent of it is obtained in the form of ammonia (corresponding to approximately 25 pounds of sulphate per ton of coal) in the production of coke in by-product ovens, it is evident that the quantity of ammonia potentially available is exceedingly large. At the present time over half of the coke produced in this country is from by-product ovens. The necessity of observing greater economy in the utilization of coal is becoming more generally recognized, and as a result the quantity of coke produced in by-product ovens is gradually becoming a larger and larger percentage of the whole. The production of by-product ammonia will therefore undoubtedly continue to increase.

At the present time, ammonium sulphate is the principal form in which fixed nitrogen, fixed in the form of ammonia, is marketed for fertilizer purposes, and it undoubtedly will continue to be so for many years. The large expansion which is expected in the future in the fixation of atmospheric nitrogen will therefore be accompanied by a large increase in synthetic ammonium sulphate.

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[4] Am. Fert. Handbook (1920), p. 112.

6. Construction and Operating Costs.

Estimates made in the latter part of 1920 for the cost of construction and installation of an ammonium sulphate plant having a capacity of 86,500 tons per annum are given in condensed form below.

	Cost per annual ton of ammonium sulphate.
Manufacturing building and machinery foundations	$4.22
Absorbing system (includes absorbers, towers, acid supply, and emergency, settling basin, troughs, and hoods)	1.50
Drying system (centrifuges, rotary driers, etc.)	1.56
Conveying equipment (elevators, conveyors, etc.)	0.33
Piping (NH_3 gas, steam, water, etc.)	1.73
Electrical equipment	.58
Storage building	4.05
Contingencies	1.48
Total	15.45

This plant was to operate 24 hours a day on pure ammonia gas obtained from cyanamide.

Other figures available at the present time are those referring to pre-war conditions in England. At that time it is estimated that the capital cost of the sulphate section of a plant for fixing a pure, strong ammonia as sulphate would cost £14.63[5] per metric ton of combined nitrogen per annum, which is equivalent to $16.57 per short ton of ammonium sulphate per annum.

It has been estimated (Appendix C) that it would cost $39.79 per short ton to produce ammonium sulphate at Muscle Shoals from ammonia gas at $100.13. This figure should be increased to $43.81 per ton to allow for bagging, sales, and miscellaneous overhead exclusive of royalties and interest. Figures calculated from English pre-war conditions[5] and derived from investigation of foreign factory costs show that ammonium sulphate is estimated to cost $34.80 per short ton with ammonia gas at the same price as above. Both of these figures are for sulphate packed for the market and do not include interest on the capital cost of the plant.

C. AMMONIUM NITRATE.

1. Introduction.

The manufacture of ammonium nitrate assumed a position of great importance during the war. The pre-war production of ammonium nitrate was relatively small. It was used principally in the manufacture of safety explosives, and to a lesser extent in the manufacture of nitrous oxide for anæsthetic purposes. Although the present consumption of ammonium nitrate is likewise quite small, there appears to be definite possibilities of a much more extensive use in the future.

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[5] Final report Nitrogen Products Committee, pp. 262 and 263. London (1920).

2. Processes of Manufacture.

Various processes for the manufacture of ammonium nitrate have been used, depending on the combination in which the ammonia and nitrate nitrogen is present. Recent developments in nitrogen fixation and ammonia oxidation have, however, resulted in the establishement of a single process to the practical exclusion of all others. This process consists in the neutralization of nitric acid by ammonia. The other processes depend on double decomposition of certain salts, such as sodium nitrate and ammonium sulphate.

a. Neutralization process.—In the neutralization process ammonia gas is passed into nitric acid and the solution evaporated until practically all of the water has been eliminated. The reaction involved is essentially as expressed by the equation

$$HNO_3+NH_3=NH_4NO_3+\text{heat.}$$

The nitric acid is obtained by the arc process of nitrogen fixation or by oxidation of ammonia and ranges in concentration from 35 to 50 per cent HNO_3. The first and last "runnings" in nitric-acid manufacture are also used quite extensively for this purpose in this country.

By-product ammonia may be used, but synthetic ammonia is to be preferred, particularly in the manufacture of ammonium nitrate for explosives, since the sulphur and organic impurities present in the by-product ammonia render the ammonium nitrate less stable. Practically all of the ammonium nitrate manufactured in this country is, however, from by-product ammonia.

The neutralization process is carried out in a manner very similar to that for ammonium sulphate using concentrated ammonia gas. It differs, however, in that the neutralized solution is not evaporated in the absorber. Ammonia gas and nitric acid are continuously fed into the inclosed neutralizing tank, the feed being so regulated that a practically neutral solution is obtained. This solution overflows into a tank where it is adjusted to neutrality.

The temperature in the absorber, or neutralizer, rises to about 100° C., due to the heat of neutralization. The steam thus generated, together with unabsorbed ammonia, passes out through the top of the neutralizer into a cooler in which the moisture is condensed, draining back into the neutralizer. To prevent loss of the unabsorbed ammonia an acid absorption tower, very similar to those used in making ammonium sulphate, is provided. The gas reaching this tower is completely neutralized by the acid fed in at the top. The resulting solution is passed into the neutralizer for complete neutralization.

After adjusting the solution to neutrality it is evaporated until it contains less than 3 per cent of water, the completeness of evaporation depending on the use to which the ammonium nitrate is put. When the water content is reduced to this amount the product is a molten salt having a freezing point of about 140° to 150° C.

For many purposes it is desirable to have the ammonium nitrate in the form of grains. This is accomplished by running the molten salt into a jacketed grainer or crystallizing kettle, in which it is continuously stirred for several hours while its temperature is properly controlled by admitting steam or cold water to the jacket. The grained product is discharged from the grainer after it reaches a temperature of about 70° C.

Attempts have been made to reduce the hygroscopicity of ammonium nitrate by coating the grains with a protective film of oil. The oil is best applied before the hot material is discharged from the grainer. This treatment will be more fully described in Chapter VI.

A modification of this process, by which the evaporation of the neutralized solution as a separate step is avoided, has been suggested,[6] but to our knowledge has not been put into practice. It depends on the use of a much stronger acid than is now produced by the arc or ammonia oxidation processes and consequently its application would be limited.

b. Double decomposition processes.—Reference has already been made to the production of ammonium nitrate by double decomposition of certain salt mixtures. These processes were used to a considerable extent before the war and quite extensively during the war. In the latter period it was impossible to meet the enormous demand for ammonium nitrate because of the shortage of nitric acid, and consequently processes which could utilize available nitrate salts were put into operation. They are, however, to be regarded more as emergency processes than as commercial ones, particularly in view of the recent developments in ammonia synthesis and oxidation.

Ammonium nitrate has been produced from both sodium nitrate and calcium nitrate. The reaction in the former case is expressed by the equation

$$2NaNO_3 + (NH_4)_2SO_4 = 2NH_4NO_3 + Na_2SO_4 \qquad (1)$$

and in the latter case by

$$Ca(NO_3)_2 + (NH_4)_2SO_4 = 2NH_4NO_3 + CaSO_4 \qquad (2)$$

or by

$$Ca(NO_3)_2 + (NH_4)_2CO_3 = 2NH_4NO_3 + CaCO_3 \qquad (3)$$

Attempts have been made to substitute sodium nitrate for sodium chloride in the ammonia-soda process and thus obtain ammonium nitrate, but it is understood these were unsuccessful due to incompleteness of reaction and difficulties in separation of the product in a sufficiently pure state.

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[6] Final report Nitrogen Products Committee, p. 272.

All of these processes involve an accurate knowledge of the phase relations existing under various conditions of temperature and concentration and require very careful control.

A plant for the production of 300 long tons of ammonium nitrate per 24 hours from sodium nitrate and ammonium sulphate (equation 1) was erected and put into operation by the Government at Perryville, Md., in 1918. Although operation was discontinued at the close of the war, it had been carried on for a sufficiently long period to demonstrate its success. This plant and process has previously been described[7] and will, therefore, not be further discussed here.

The manufacture of ammonium nitrate by double decomposition of calcium nitrate (Norwegian saltpeter) and ammonium sulphate was carried out in a number of countries during the war. The Norwegian product was imported by England for this purpose during the early period of the war, but it is understood that it was later displaced by Chilean nitrate.

3. Plant Equipment.

The manufacture of ammonium nitrate requires equipment of a special material and construction, due to the corrosive action of the solutions handled, particularly at the higher temperature.

The installation at United States Nitrate Plant No. 2 consists of four units, each having a rated capacity of 100 tons of ammonium nitrate per 24 hours. A neutralizer unit consists of an acid supply tank, absorption tower, cooler, neutralizing tank or absorber, and an adjusting tank, together with wells for acid air lifts.

The neutralizers are aluminum tanks lined with acid-proof brick. The coolers, placed between the neutralizer and the absorption tower, are quite similar to the low-temperature coolers for gases from the ammonia oxidizers and contain duriron cooling tubes. The absorption towers, which are set in aluminum trays, are of acid-proof brick and are packed with spiral tile. The acid is distributed at the top from the aluminum acid-supply tanks by means of a stoneware spray. The adjusting tanks are open steel tanks lined with acid-proof brick.

The evaporating and graining installation is divided into five units, each having a rated capacity of 60 tons of ammonium nitrate per 24 hours. A unit contains 10 evaporating pans and 20 graining or crystallizing kettles. The pans are of Elyria ware and are provided with aluminum steam and air agitation coils. The Buflokast graining kettles used are provided with a steam and water jacket.

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[7] Chem. and Met. Eng., 20; 320 and 401 (1919).

4. Present Status of the Industry.

Figures as to the world's present production of ammonium nitrate are not available. It is probable, however, that it is being manufactured on a large scale only in Germany and, to a lesser extent, in Norway.

The plants in Germany are undoubtedly operating at least to the extent of furnishing the ammonium nitrate required for industrial explosives, and it is understood that some ammonium nitrate is also being used as fertilizer. Germany has three ammonia oxidation plants, having a combined capacity of 53,000 tons of nitrogen per annum, and consequently is in a position to produce very large quantities of ammonium nitrate.

Ammonium nitrate is now being manufactured in Norway, but information as to the output is not available. In 1920 the quantity of this material exported from Norway amounted to 20,244 metric tons.[8] The manufacture of ammonium nitrate in that country has been carried out by operation of the cyanamide-ammonia process in conjunction with the arc process.

5. Demand for Product and Future Outlook.

The present production capacity for ammonium nitrate far exceeds the demands, due to the great stimulation which this industry received during the war.

The principal peace-time use for ammonium nitrate is in the manufacture of safety explosives, although the quantity so used is relatively small. It has been estimated, for example, that the total quantity of ammonium nitrate used in permissible explosives in this country during 1920 amounts to approximately 16,000 tons.[9] It is probable that the total consumption in this country for all purposes in 1920 did not exceed 25,000 tons.

There appears to be no possibility of a decided increase in the peace-time requirements for ammonium nitrate except for fertilizer purposes.

The fixation of ammonia as ammonium nitrate has some advantage over the production of ammonium sulphate. It contains a high percentage of nitrogen, which is an advantage if it is to be shipped long distances. One-half of the nitrogen is in the nitrate form, which is also an advantage from the agricultural standpoint. No outside source of acid is required. However, there are disadvantages also. The nitrogen losses are greater in making ammonium nitrate than in making sulphate, and operation of the process is more expensive. In its physical properties ammonium nitrate is not as desirable as ammonium sulphate for use in fertilizer and is not as well known to the fertilizer trade as is ammonium sulphate.

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[8] Statistical Supplement, Final Report, Nitrogen Products Committee, p. 15, Table XVIII.

[9] Production of Explosives in the United States during 1920. Bureau of Mines Technical Paper 291, p. 21.

Many attempts have been made to reduce the hygroscopicity of this salt so as to permit its use as fertilizer. Some of these have met with a certain measure of success, as will be further mentioned in Chapter VI.

An extensive use of ammonium nitrate in the future is contingent on the satisfactory solution of the hygroscopicity problem.

6. Construction and Operating Costs.

The construction cost of the ammonium nitrate plant of 110,000 tons per year capacity, at United States Nitrate Plant No. 2, exclusive of raw material, storage, and auxiliaries, and of facilities for furnishing steam, power, and water, was $1,234,000, or $11.22 per annual ton of product. If it is assumed that present-day reproduction of this plant could be made at 60 per cent of its war-time cost, this cost is reduced to $6.73 per annual ton of ammonium nitrate.

The manufacturing cost has been estimated (Appendix C) at $60.78 per short ton, using ammonia gas at $100.13 and nitric acid at $37.98 per ton.

D. OTHER NITROGEN CONVERSION PROCESSES.

Nitrogen conversion processes which are of lesser importance at the present time than the ones just described, but which are, nevertheless, of growing commercial significance in the nitrogen industry, will be considered here.

1. Manufacture of Ammonium Phosphate.

Ammonium phosphate is produced by the absorption of ammonia gas in phosphoric acid. Of the three ammonium phosphates—mono, di, and tri—only the first is stable under ordinary conditions and is therefore the only one which has large commercial possibilities.

Monoammonium phosphate, under the trade name of "Ammo-Phos," has been produced to a considerable extent by the American Cyanamid Co. for the export trade where the saving in freight rates is enough to compensate for the increased cost of manufacture over that of an equivalent amount of ammonium sulphate and acid phosphate.

The phosphoric acid in the process of the American Cyanamid Co. is the relatively expensive and *dilute* phosphoric acid, which can be obtained by the treatment of phosphate rock with sulphuric acid. Further extensions in the commercially successful production of ammonium phosphate will probably be dependent on the production of cheap concentrated phosphoric acid by thermal or electrothermal methods. It is probable that economical methods of doing this will soon be available.

The manufacture of ammonium phosphate on a large scale using *concentrated* acid has not been carried out. Laboratory investigations indicate, however, that the process will very closely correspond in operation and equipment to that for the manufacture of ammonium sulphate using concentrated ammonia gas.

Monoammonium phosphate possesses many advantages as a fertilizer salt. It is stable, nonhygroscopic, of very satisfactory physical condition, is a concentrated plant food (about 12 per cent N and 60 per cent P_2O_5), and has proven to be entirely satisfactory in the agricultural experiments thus far made. This salt undoubtedly possesses great possibilities as a fertilizer material.

2. Manufacture of Urea.

Urea is now being manufactured on a limited scale by two processes, namely, from ammonia and carbon dioxide and by the hydrolysis of cyanamide. The former is quite fully described in Chapter VI. It is in operation on a limited scale in Germany.

The process of producing urea from calcium cyanamide is briefly as follows: The crude calcium cyanamide is extracted with cold water, the solution filtered off, a quantity of sulphuric acid added in excess of that required to precipitate all the calcium, the solution heated to hasten hydrolysis of the free cyanamide to urea, and the excess acid then precipitated as a calcium salt. The solution is then filtered to remove the calcium sulphate and evaporated under reduced pressure to avoid decomposition of urea. Temperature control is an important factor in avoiding the formation of dicyanodiamide.

The product thus produced contains a small quantity of calcium sulphate as an impurity. The successive treatment of the solution with barium hydroxide and oxalic acid before evaporation will reduce the impurity to a negligible amount. The product may also be purified by recrystallization from alcohol.

The sludge remaining after extraction still contains some nitrogen, and it may therefore be desirable under certain circumstances to recover it in the form of ammonia by autoclaving.

The cost of sulphuric acid used in the process is an important item in the cost of conversion. The acid is converted into calcium sulphate and consequently is entirely lost in the process. The use of nitric acid and of phosphoric acid[10] has been suggested instead of sulphuric acid. Both are known to be satisfactory in hydrolyzing cyanamide to urea, and it appears probable that the resulting mixture of salts, such as urea nitrate, calcium nitrate, calcium nitrate-urea,[11] urea phosphate, calcium phosphate, etc., could be used directly as fertilizer if production costs would be made low enough.

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[10] U. S. patent 1,355,369.

Due to the high price of urea, its use is limited very largely to the manufacture of high-grade materials, such as celluloid products and medicinal preparations. Urea contains about 46 per cent nitrogen, and appears to be an excellent fertilizer material. Its very extensive use for that purpose, therefore, appears to be contingent only on sufficiently low costs of manufacture.

3. Production of Cyanide From Calcium Cyanamide.

Cyanide is produced from crude calcium cyanamide by strongly heating the latter in the presence of free carbon with a flux such as sodium chloride. There is some doubt as to the reactions taking place and the composition of the product, but it is generally believed that calcium cyanide is formed essentially as is shown by the equation

$$CaCN_2+C=Ca(CN)_2,$$

the salt merely acting as a fluxing agent.

The process was studied by Frank and Caro and their associates as early as 1900, and patents relating to it were obtained shortly thereafter. It is understood, however, that the process was abandoned in Germany after many years of experimentation.

A plant for the production of cyanide from calcium cyanamide was erected by the American Cyanamid Co. at Niagara Falls in December, 1916. The process[12] consists essentially in continuously feeding a mixture of cyanamide and sodium chloride into a single-phase electric furnace having a conducting hearth and a single suspended electrode, maintaining the molten charge at a temperature of about 1,300° C. for about an hour, and quickly chilling the continuously discharged product, so as to prevent reversal of the reaction.

The crude cyanide thus obtained consists of thin flakes of grayish-black material containing from 35 to 50 per cent equivalent of sodium cyanide, the percentage depending largely on the composition of the charge. It is stated that a 90 per cent conversion of nitrogen in cyanamide to cyanide is regularly obtained in making a 37 per cent product.

The product is generally marketed in two grades, 37 and 45 per cent sodium cyanide equivalent. It has been successfully used in gold and silver metallurgy and in the manufacture of hydrocyanic acid for fumigation purposes.

Figures on the cost of production are not available, but it is probable that they are quite low. There would seem to be a good future for this material in operations where the crude product may be used, as for the production of liquid hydrocyanic acid. For this latter purpose it can undoubtedly compete with hydrocyanic acid made from sodium cyanide.

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[11] U. S. patent 1,369,383.

[12] Chem. and Met. Eng., 22: 265 (1920).

4. Conversion Products of Cyanamide.

The production of ammonia, cyanide, and urea from crude cyanamide has already been described. A large number of other compounds of increasing importance can also be obtained from the same source. Among the more important of these are free cyanamide, H_2CN_2, dicyanodiamide $(H_2CN_2)_2$, and guanidine, H_5CN_3. The methods of obtaining these from cyanamide are described in Chapter VI.

The use of these compounds up to the present time has been very limited, due to their high cost. Free cyanamide, for example, has not been on the market in this country; dicyanodiamide of fair degree of purity commands a price of about $2 per pound, while guanidine in the form of the hydrochloride was quoted at about $35 per pound in 1920. By employing methods which have recently been developed all of them can be prepared from crude cyanamide for a very small fraction of their present cost. These illustrations serve to indicate the great possibilities of crude cyanamide as a raw material for organic syntheses. Further reference to these possibilities is made in Chapter VI, section C–6.

5. Miscellaneous Nitrogen-Containing Salts.

The conversion of various salts into states of combination which have certain advantages, particularly for fertilizer purposes, has been given considerable attention.

Double and mixed salts of ammonium nitrate have been prepared in an attempt to utilize this compound as a fertilizer. It forms two double salts with ammonium sulphate, which have the composition $(NH_4)_2SO_4.2NH_4NO_3$ and $(NH_4)_2SO_4.3NH_4NO_3$. The former is considerably less hygroscopic than ammonium nitrate and has been manufactured for fertilizer purposes in Germany to a considerable extent. The second double salt is very hygroscopic.

Mixed salts obtained by double decomposition of ammonium nitrate with potassium chloride and with potassium sulphate are sufficiently nonhygroscopic for fertilizer salts when fairly high grade potash salts are used. The mixed salts are now being manufactured in Germany.

Urea forms a double salt with calcium nitrate having the composition $Ca(NO_3)_2.4CO(NH_2)_2$. It also forms stable salts with nitric and phosphoric acids in monomolecular proportions. Urea and its salts here mentioned are nonhygroscopic. As far as is known they are not yet being used as fertilizer materials, but it appears possible that they may eventually be used for that purpose.

CHAPTER VI.

RESEARCH.

A. NECESSITY FOR RESEARCH.

The importance of nitrogen fixation for national welfare, the novelty of existing fixation processes with the opportunities presented for their further improvement, the considerable possibility that completely new processes can be brought to successful commercial development, and the variety of new products made available by nitrogen fixation, all contribute to an imperative necessity for scientific research.

1. Importance of Nitrogen Fixation for National Welfare.

The problem of nitrogen fixation is quite evidently one of vital national importance both in war and in peace. The element forms an essential constituent of explosives, of fertilizers, of dyestuffs, and of many other substances used in the arts. In time of war the country must depend for its increased need for explosives on nitrogen fixation or on the importation of Chilean saltpeter, with its attendant uncertainties and tie-up of transportation. In time of peace the use of nitrogen in fertilizers is only limited by the supply, and if available, larger quantities would be used for increasing the food and other crops necessary for the country's welfare.

The nitrogen-containing explosives necessary to keep an army of 50 divisions in the field for one year have a value of approximately $500,000,000. Professor Whitney, chief of the Bureau of Soils, estimates that it would require 772,000 tons of additional ammonia to bring the application of commercial fertilizer throughout the United States up to the standard now prevailing in the State of Georgia, of 160 pounds of fertilizer to the acre, compared with the pre-war use of 162 pounds to the acre in Great Britain and 188 pounds to the acre in Germany. It will be a long time before such an additional tonnage of ammonia will be used for agriculture; nevertheless, the figures set an interesting limit. This additional ammonia would be 15 times the capacity of the Muscle Shoals plant, and at $240 a ton it would have a value of $185,000,000. These figures alone demonstrate the importance of nitrogen fixation to national well-being and justify the prosecution of governmental research in this field. Indeed, as Professor Shimer, of the Massachusetts Institute of Technology, has put it, man has passed through the stone age, the bronze age, and the iron age, and now is in the nitrogen age.

2. The Novelty of Existing Processes of Nitrogen Fixation.

The art of nitrogen fixation is a relatively new one. The oldest of all the successful processes—the arc process—was first tried out on a large scale by Bradley and Lovejoy at Niagara Falls in 1902 and in Norway by Birkland and Eyde in 1903; the cyanamide process was first put in operation in Piano d'Orta, Italy, in 1906, and at the present time the Haber process, with the exception of the plant at Syracuse, N. Y., has never been in large scale operation outside of Germany. This novelty of the existing processes leaves a large field for improvement, and it is believed that further research can lead to important lowerings of cost, as will be indicated in a later section.

3. Possibility of New Processes.

Besides the three standard methods of nitorgen fixation which have been brought to commercial success, we have already described in Chapter IV a number of other methods which appear promising. The most important of these is perhaps the cyanide process, and further investigations of the chemical reactions involved in this process should be made, since our present information in this field is incomplete and in some instances apparently faulty. The aluminum-nitride process, the magnesium-cyanamide process, and a number of others are also worthy of further research.

4. New Nitrogen-Containing Substances.

Before the development of nitrogen fixation the most important forms of inorganic fixed nitrogen were sodium nitrate obtained from Chile under the name of Chilean saltpeter and ammonium sulphate obtained as a coke oven by-product. The development of nitrogen fixation, however, has led directly or indirectly to a supply of a number of new substances. Thus the arc process has furnished as its principal product calcium nitrate or "Norwegian saltpeter;" the cyanamide process has given us the new substance, calcium cyanamide, with a great variety of derivatives, such as dicyanodiamide, guanylurea, guanidine, nitroguanidine, etc., and both the cyanamide process and the Haber process present the possibility of producing ammonium nitrate, ammonium phosphate, urea, and other compounds. Research is needed on all of these substances from the point of view of their utilization in agriculture, explosives, or the arts, and from the point of view of their transformation from one form into another.

B. WORK OF THE FIXED NITROGEN RESEARCH LABORATORY.

The necessity for research in the field of nitrogen fixation has been appreciated by the Government for a number of years. Experimental work on the fixation of nitrogen by the arc process and the Haber process was started as early as 1915 by the Bureau of Soils of the Department of Agriculture under the direction of Prof. Milton Whitney. During the war nitrogen research was carried out in a variety of fields by the technical research branch of the Nitrate Division, Ordnance Department, under the direction of Lieut. Col. Alfred H. White, in cooperation with the Bureau of Soils, the Geophysical Laboratory, the Bureau of Mines, the Bureau of Standards, and a number of other agencies. At the close of the war governmental research on nitrogen fixation was concentrated at the Fixed Nitrogen Research Laboratory, Washington, D. C., founded by an order of the Secretary of War March 29, 1919. This laboratory, cooperating with the Bureau of Soils, has continued work until the present time, with a total personnel in the neighborhood of 115 employees and an annual budget in the neighborhood of $280,000. On June 30, 1921, the laboratory was transferred to the Department of Agriculture.

The purpose of the following section is to describe in a very general way the results already achieved by the Fixed Nitrogen Research Laboratory.[1] Most of this material has been presented to the Chief of Ordnance in the form of confidential reports, but some of it has already been published, and in the future it is expected that the policy of publication will be greatly extended. In what follows we shall merely make statements as to the most important conclusions which have been obtained from the work of the laboratory without any detailed description as to the experimental methods employed. Experiments which have led to negative results will be described as well as those which have had a successful outcome, because of their importance in indicating lines of attack which can not be profitably undertaken by future investigators.

1. The Direct Synthetic or Haber Process.

Owing to the Government ownership of United States Nitrate Plant No. 1, at Sheffield, Ala., designed to operate in accordance with a modified Haber process, the laboratory has devoted a very considerable amount of energy to an investigation of this process. The Sheffield plant was not a success, and this was partly due to insufficient technical information in connection with the various physical-chemical steps which go to make up the process. It has been the function of the laboratory to supply this missing technical information, and the results already obtained are briefly described below. Since the Government no longer plans to reconstruct plant No. 1, it is hoped that these results will be of use to the nitrogen industry in general. The investigations are described in the same order as that of the several steps in the process to which they apply.

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[1] The results described include the work of the laboratory up until November, 1921.

a. Catalyst for the production of hydrogen from carbon monoxide and steam.—In the special form of Haber process installed at Sheffield, the so-called Haber-Bosch process, water gas from gas producers is made the source of the hydrogen. About 20 per cent of the total cost of the process goes into the production of this water gas and about 50 per cent of the total cost goes into the changes which must be brought about in the water-gas mixture before it is ready for circulation through the ammonia synthesizing catalyst. The first step in these changes is the passage of the water-gas mixture, together with an excess of steam, through a catalyst, which causes the following reaction to take place:

$$CO+H_2O=CO_2+H_2.$$

Since the original water gas contains approximately equal parts of carbon monoxide and hydrogen, we thus nearly double the amount of hydrogen.

The catalyst which has been most commonly used for the above reaction has been iron oxide containing cerium oxide and chromium oxide as promoters. The laboratory has developed a satisfactory method for testing such catalysts and has commenced tests upon them. The results already obtained show that the success of such catalysts is markedly dependent on their method of preparation and consequent physical structure. Catalysts prepared by fusion of the oxides are not satisfactory owing to low activity. Catalysts prepared by precipitation are often unsatisfactory owing to lack of stability of the granules. Thus tests made on a sample of a commercial catalyst which had been made by precipitation showed that the granules disintegrated very badly in the course of a 24-hour test, producing a large amount of fines. By the use of a special technique, however, the laboratory has developed a satisfactory precipitated catalyst which will not disintegrate in use.

The precipitation of the iron oxide for this catalyst is carried out by a method developed in 1918 by the Research Division of Chemical Warfare Service. A 5 to 6 per cent ferric salt solution at 40° to 50° C. is poured into a slight excess of 5.8 per cent ammonia solution at the same temperature. The mixture is stirred vigorously during precipitation, allowed to settle, and the supernatant solution siphoned off. The precipitate is then thoroughly washed by decantation, filtered, and introduced into a kneading machine, together with the desired promoters present either as oxides or nitrates. After thorough kneading the material is again filtered to remove the solution expelled by the kneading, the filter cake broken into 1-inch cubes and dried in an air-ventilated oven at 80° to 90° C. for 12 hours and then at 125° to 150° for 24 hours.

By this technique a catalyst has been obtained so active that when a mixture of 1 part of water gas (50 per cent CO) and 6.2 parts of steam is passed over it at 1,000 space-velocity (liters of gas per liter of catalyst per hour) the resulting gas, after removal of the excess steam, contains only 1.96 parts of carbon monoxide and 98.04 parts of hydrogen.

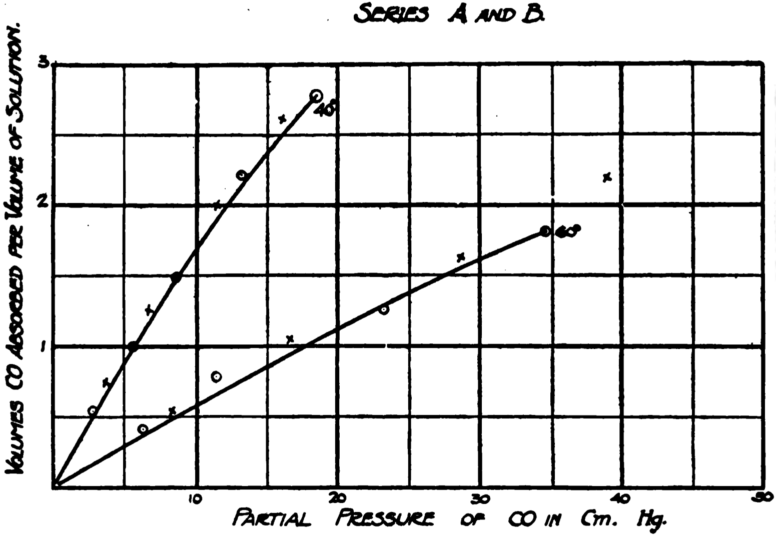
Work on the problem has only begun, and the above data is merely given as an example of the type of results to be expected. The catalyst has not yet been tested over a wide range of space velocities nor against poisons.

b. Removal of carbon monoxide by cuprous solutions.—Since all known catalysts for the production of ammonia from nitrogen and hydrogen are either permanently destroyed or temporarily poisoned by carbon monoxide, the removal of the small percentage of carbon monoxide left in the gas after the above reaction is very important. In the case of satisfactory ammonia catalysts which operate at low temperature and are not permanently destroyed by carbon monoxide, 0.1 per cent CO may cause a temporary decrease in the per cent of ammonia synthesized of as much as 60 to 70 per cent of that formed from pure gas. Hence the necessity for as complete removal of carbon monoxide as possible will be readily appreciated.

The method usually proposed for carbon monoxide removal has been that of "scrubbing" the gas with ammoniacal cuprous solutions. In connection with the development of such a scrubbing process, the Fixed Nitrogen Research Laboratory has studied the solubility of carbon monoxide in ammoniacal solutions, both of cuprous carbonate and cuprous formate. The general nature of the results indicate that the process to be employed for carbon monoxide removal should consist of low temperature scrubbing, using a countercurrent flow of gas and cuprous solution followed by high temperature regeneration of the scrubbing solution. In connection with such a proposed method the following points have been established by the work.

1. The solubility of carbon monoxide in solutions containing equivalent concentrations of ammoniacal cuprous carbonate and ammoniacal cuprous formate is the same. (See fig. 6.)

2. Cuprous formate, although more expensive than cuprous carbonate, is more satisfactory as an absorbent, since its decomposition with precipitation of metallic copper is very much less. Thus, in the experiments shown on figure 6, the solutions were kept at 40° and at 60° C. for a day and a half each. During this time 5.3 per cent of the total copper present was precipitated from the carbonate solutions



COMPOSITION IN Gm PER 100 cc.			
SERIES A		SERIES B	
Cu	4.90	Cu	5.08
NH_3 (FREE)	5.26	NH_3 (FREE)	5.04
$(NH_4)_2CO_3$	14.81	NH_4OOCH	17.95
CO_2	6.77	HOOCH	13.10
TOTAL NH_3	11.80	TOTAL NH_3	11.25
Cu p'p't'd. IN THIS RUN	.26	Cu p'p't'd. IN THIS RUN	VERY SLIGHT

NOTE:-
POINTS SERIES A - x
POINTS SERIES B - ⊙

FIGURE 6

and only a trace from the formate solution. The rate of precipitation increases rapidly with the temperature.

Ammoniacal cuprous formate is also to be preferred to ammoniacal cuprous carbonate, since the latter decomposes with evolution of carbon dioxide at regeneration temperatures.

3. The solubility of carbon monoxide is greatly decreased with rise in temperature. (See fig. 7.) It would seem as if 0° C. would be a satisfactory temperature for the operation of the scrubber and 60° for the regenerator.

4. The amount of carbon monoxide absorbed approaches a limiting value at high partial pressures of carbon monoxide, and this limit is independent of the concentration of free ammonia in the solution, but the solubility at low partial pressure is increased by the concentration of free ammonia. (See fig. 7.) Hence high ammonia concentration is valuable in removing the last traces of carbon monoxide. A practical limit, however, is set to the concentration of ammonia by the loss of ammonia in the regenerator.

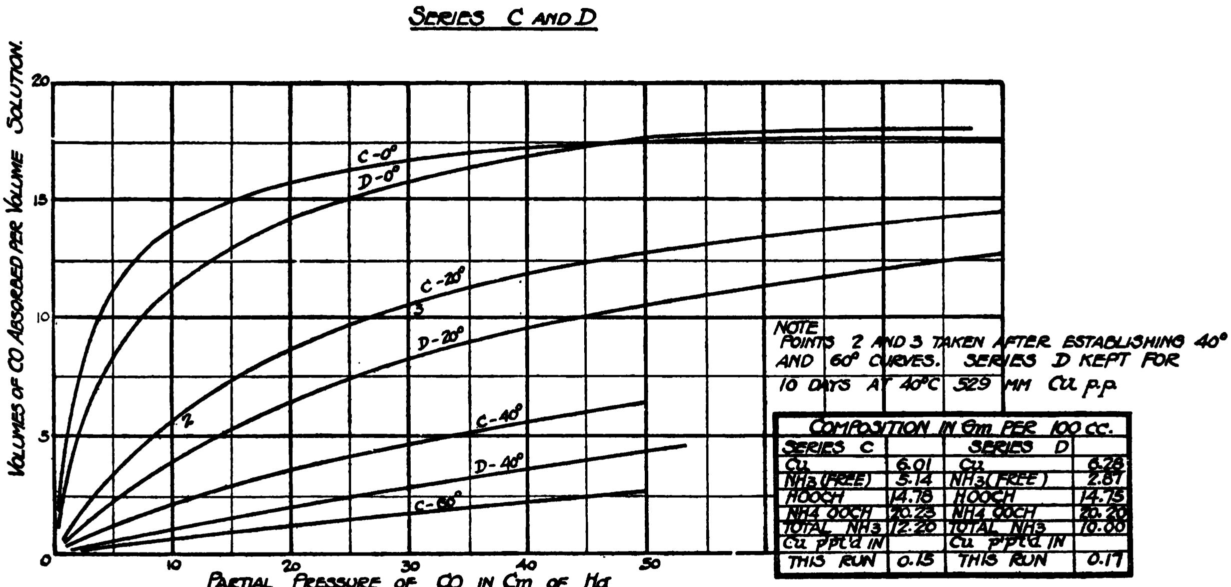
5. The limiting value of the carbon monoxide absorbed at high partial pressures of that gas increases proportionally to the copper content of the solution, and the solubility at low pressures is also increased by increase in copper content. Hence for both reasons a high copper content is desirable. A practical upper limit is set, however, by the precipitation of copper at the high temperature in the regenerator.

6. Copper precipitated in the regenerator can be removed by the use of hot cupric solutions.

c. Removal of carbon monoxide by differential oxidation.—In connection with the removal of carbon monoxide from the nitrogen-hydrogen mixture used in the Haber process, mention should be made of some work on removal by differential oxidation, made by the Research Division, Chemical Warfare Service, working in cooperation with the Nitrate Division of the Ordnance Department previous to the formation of the Fixed Nitrogen Research Laboratory.

As a result of this work, a number of oxidation catalysts have been prepared which at temperatures in the neighborhood of 100° will bring about a differential oxidation of carbon monoxide in the presence of hydrogen. By using twice the theoretical amount of oxygen necessary to oxidize the carbon monoxide present it is possible to reduce the carbon monoxide concentration to less than 0.01 per cent. The excess oxygen combines with hydrogen to form water.

The temperature control for such a process would be a matter of great difficulty, since under given conditions of concentration and space velocity it has been found necessary to maintain the catalyst within a definite temperature interval of about 25° in order to remove carbon monoxide to the figure mentioned above. No large-scale



NOTE
POINTS 2 AND 3 TAKEN AFTER ESTABLISHING 40° AND 60° CURVES. SERIES D KEPT FOR 10 DAYS AT 40°C 529 MM Cu p.p.

COMPOSITION IN Gm PER 100 CC.			
SERIES C		SERIES D	
Cu	6.01	Cu	6.28
NH_3 (FREE)	5.14	NH_3 (FREE)	2.87
HOOCH	14.78	HOOCH	14.75
NH_4 OOCH	20.23	NH_4 OOCH	20.20
TOTAL NH_3	12.20	TOTAL NH_3	10.00
Cu ppt'd IN THIS RUN	0.15	Cu ppt'd IN THIS RUN	0.17

FIGURE 7

experiments have been made for developing the necessary method of temperature control.

d. Detection and analysis of impurities in nitrogen-hydrogen mixtures.—The catalyst poisons most difficult to detect and estimate which may occur in the nitrogen-hydrogen mixture used in the Haber process are oxygen, water vapor, carbon monoxide, and volatile hydrocarbons which may come from the lubricant used in the compressors.

For the detection and rough estimation of water vapor and hydrocarbons the laboratory has found the use of liquid air very satisfactory. The gas to be tested is passed through a coil of glass whose lower turns are immersed in liquid air. Water vapor condenses in the upper turns and very volatile hydrocarbons lower down. The method is very rapid and exceedingly informing.

It has been found that the direct analysis for water vapor with phosphorous pentoxide in the final dried and purified gas is not satisfactory, owing to the low concentrations of water present. A preliminary precipitation of water vapor by the liquid-air method followed by reevaporation in a *small* volume of air and analysis by the phosphorous pentoxide method would undoubtedly lead to satisfactory results.

For the estimation of oxygen, the laboratory has developed a method similar to that of Lamb and Larson (J. Amer. Chem. Soc. 41: 1908 (1919)) for the determination of traces of carbon monoxide in oxygen. The method depends on a measurement of the temperature rise produced by making the trace of oxygen combine in the presence of a catalyst with the hydrogen in the Haber process gas. A very neat method of calibrating the apparatus has been developed by the use of an electrolytic cell furnishing a known quantity of oxygen in accordance with Faraday's law. The method permits the analysis of a gas containing 0.001 per cent oxygen. It is expected that a detailed discussion of the method will be published in the Journal of the American Chemical Society.

For the estimation of carbon monoxide the laboratory has found it possible to use the well-known iodine pentoxide method. It is necessary to prepare the iodine pentoxide by the oxidation of iodine with chloric acid as described by Lamb, Bray, and Geldard (J. Amer. Chem. Soc. 42: 1636 (1920)).

e. Methods of testing ammonia catalysts.—Although about 70 per cent of the cost of carrying out the Haber-Bosch process occurs before the gases are ready to enter the circulating system containing the catalyst, nevertheless the catalyst for the synthesis of ammonia must be considered as the heart of the process, since the whole design of the plant and the most economical method of operating depend upon the yield of ammonia which can be obtained by passing the gases at different velocities and temperatures through the particular catalyst selected.

The Fixed Nitrogen Research Laboratory has developed somewhat elaborate methods for testing ammonia catalysts on a *small* scale at pressures from 1 to 100 atmospheres and on a *moderate* scale at 100 atmospheres pressure.

The apparatus and methods involved are so elaborate that no detailed description of them can be given here. It may be said, however, that the laboratory has solved with reasonable success the problems of securing a supply of pure nitrogen-hydrogen mixture for carrying out the tests, of introducing known concentrations of water vapor and carbon monoxide when the catalysts are to be tested against poisons, of controlling the temperature and velocity of flow during the test, and of eliminating temperature gradients in the catalyst samples under test.

Nine units are available for testing catalysts on a small scale at 1 atmosphere, 8 units for testing on a small scale at pressures from 1 to 100 atmospheres, and 8 units for testing catalysts on a moderate scale at 100 atmospheres pressure. These latter units are kept running night and day and the plant has been in continuous operation since March 20, 1920, thus permitting tests of the effective life of the catalyst.

It is expected that a detailed description of the testing equipment will be published in the near future. Up to the present the apparatus has been largely used for making tests on catalysts developed at the Fixed Nitrogen Research Laboratory, although some testing has been done for outside companies, and the laboratory is always ready to carry out a reasonable amount of such experimentation.

f. The preparation of iron catalysts.—Although an enormous number of materials have been tried or patented as catalysts for ammonia synthesis, successful ones have all consisted of iron containing small additions of materials called promoters. These catalysts are in general prepared by the reduction of iron oxide containing the desired promoter substance. The oxide can be prepared either by precipitation or by the fusion of iron in an oxygen blast. The oxides may be reduced with the same mixture of nitrogen and hydrogen from which ammonia is to be formed, and if desired in the same bomb or converter in which the ammonia synthesis is later to be carried out.

The laboratory has found in the preparation of iron catalysts by the precipitation method that the precipitation may be advantageously carried out by the method already described in section a for the preparation of iron oxide for the reaction between carbon monoxide and steam.

Fused iron oxides may be prepared by burning metallic iron in a stream of oxygen. The technique developed by the laboratory is essentially as follows: Five hundred grams of pure wrought-iron rod (Swedish or Armco), one-fourth or three-eighths inch in diameter, is melted in the flame of an oxyhydrogen torch with a large excess of oxygen. The drippings are caught in a pure iron cup, 3 inches deep by 3½ inches in diameter, supported by a short piece of iron pipe closed at the lower end by a cap and packed with iron oxide fines (20 to 24 mesh). A stream of oxygen is then directed into the partially oxidized mass, the reaction being started if necessary by the oxyhydrogen torch. When the mass has become sufficiently fluid it is stirred with a pure iron rod until oxidation ceases. This is indicated by the rapid formation of a crust under the oxygen jet. With the proper care the iron cup will not be destroyed during the oxidation, but even if this occurs the iron oxide fines prevent the molten material from coming in contact with the outside iron pipe. The mass after cooling is crushed and screened to the desired size. If catalysts containing promoters are desired, the promoter substance may be present in the original iron rods or stirred into the iron after fusion.

The methods of catalyst preparation briefly described above are suitable for laboratory batches.

g. The behavior of pure iron as a catalyst.—It has been found that pure iron itself, when prepared with proper physical characteristics, has a very considerable catalytic activity. Indeed, at pressures in the neighborhood of 1 atmosphere the yield of ammonia from pure iron catalysts is nearly as good as from any catalytic material that we have been able to prepare. At higher pressures, however, such as have to be used in order to obtain yields of commercial significance, the addition of promoters to the iron has been found necessary.

h. The behavior of iron containing promoters disclosed in the literature.—A very large number of elements have been suggested as suitable promoters for addition to iron catalysts, and the following elements have been patented for that purpose (U. S. patent No. 1148570): Magnesium, beryllium, aluminum, cerium, lanthanum, erbium, neodynium, praesodynium, samarium, yttrium, ytterbium, potassium, rubidium, caesium, sodium, lithium, strontium, calcium, uranium, thorium, zirconium, vanadium, niobium, tantalum, chromium, manganese, molybdenum, and tungsten.

With the exception of the relatively rare erbium, neodynium, praesodinium, samarium, yttrium, ytterbium, rubidium, niobium, and tantalum, which have not yet been tried, the laboratory has prepared catalysts by the fusion method containing each of the above elements, the promoter in the form of its oxide being stirred into the molten iron oxide. All of these promoters produced catalysts which, operating at 30 atmospheres pressure, were poorer than the catalysts that can be obtained by the addition of satisfactory promoters which will be discussed in a later section. Many of these so-called promoter substances were actually found to reduce the yield below that which can be obtained from pure iron. It seems evident that the patented promoters are not of commercial significance.

i. The behavior of iron catalysts containing a satisfactory promoter.—A number of catalysts have been prepared by this laboratory containing what may be called "satisfactory" promoters, the term being used to refer to promoters which confer upon the iron the properties of (1) maintaining a high activity, even at high pressures, and (2) operating for considerable lengths of time at temperatures as high as 550° C. without undergoing appreciable deterioration. With such catalysts as much as 16.5 per cent NH_3 may be obtained at 100 atmospheres pressure and 5,000 space-velocity (liters per hour per liter of catalyst). This type of catalyst has been studied with a great deal of care and over a wide range of conditions, and it has been found possible to draw many general conclusions concerning the effect upon such catalysts of temperature, pressure, rate of flow of gases, and poisons. Although it is not possible in a brief space to enter into many details in such a complicated problem, the conclusions stated below and the curves in figure 8 may serve to illustrate the nature of the results obtained.

It has been found that the ratio of the actual NH_3 produced to that theoretically possible under the particular conditions studied (defined as the "efficiency") in general (1) increases with increasing temperature; (2) decreases slowly with increasing rate of flow of gases; (3) decreases slowly with increasing pressure; and (4) decreases rapidly with increasing concentration of catalyst poison (water vapor or carbon monoxide). The actual per cent of ammonia produced; the optimum temperature of operation; the increase in the weight of NH_3 produced per hour with increasing rate of flow of gases; and other factors bearing upon the suitability of the catalyst for commercial operation have also been studied in much detail.

In figure 8 typical curves are drawn illustrating a few of the results obtained with an individual catalyst.

Curve 1 shows the effect of temperature upon the per cent of NH_3 (at 100 atmospheric pressure and 5,000 space-velocity), illustrating the fact that there is an optimum temperature (in this case about 450° C.) of operation, at which the highest per cent of ammonia is formed.

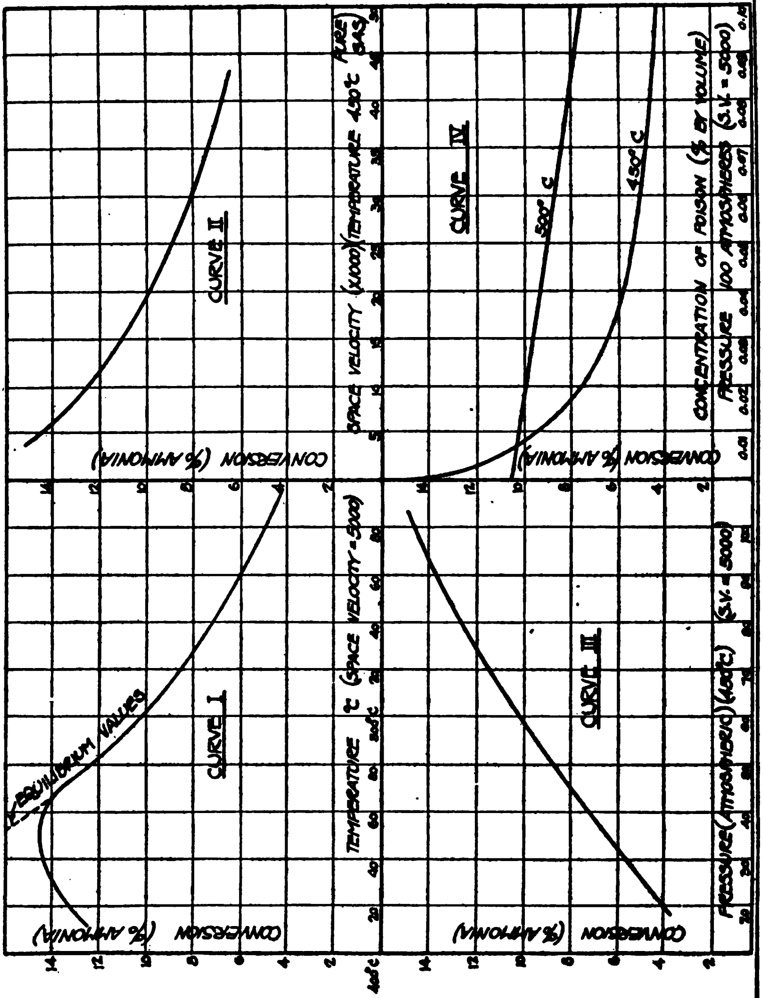

CURVE I
CURVE II
CURVE III
CURVE IV
EQUILIBRIUM VALUES
CONVERSION (% AMMONIA)
TEMPERATURE °C (SPACE VELOCITY = 5000)
SPACE VELOCITY (X1000) (TEMPERATURE 450°C)
PURE GAS
CONCENTRATION OF POISON (% BY VOLUME)
PRESSURE 100 ATMOSPHERES (S.V. = 5000)
PRESSURE (ATMOSPHERIC) (450°C) (S.V. = 5000)
500° C
450° C
14
12
10
8
6
4
2
400°C
20
40
60
80
300°C
20
40
60
80
100
5
10
15
20
25
30
35
40
45
50
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10

FIGURE 8

Curve 2 shows the effect of increasing rate of flow of gases in decreasing the per cent of NH_3.

Curve 3 shows the effect of pressure in increasing the per cent of NH_3.

Curve 4 shows the effect of concentration of catalyst poison (water vapor) in lowering the per cent of NH_3.

It has been found that catalysts of the type in question will maintain their activity indefinitely at temperatures below 550° when tested upon pure dry gas. They suffer a slow permanent deterioration in the presence of catalyst poisons, especially when tested at high pressures.

Altogether the data available concerning this type of catalyst are sufficiently complete to permit intelligent consideration of the use of such catalysts for commercial ammonia synthesis.

j. Ammonia catalysts other than iron.—The laboratory has also carried out limited tests with a number of materials besides iron as catalysts for the ammonia synthesis. These have included cobalt, nickel, and their mixtures with iron, and mixtures of iron and molybdenum; but none of these materials have given results as good as iron with a suitable promoter, and usually have been far inferior to pure iron.

k. Theory of ammonia catalysis.—A very considerable number of measurements have been made to determine the amount of nitrogen, hydrogen, and ammonia taken up by good and poor catalysts under various conditions of temperature, pressure, and concentration. Experiments have also been made on the behavior of catalysts when the flow of gas is varied in composition from 3-to-1 mixture to pure hydrogen or pure nitrogen. These tests have been devised for the purpose of throwing light on the mechanism of ammonia catalysts—at the present time they are still in progress and any statement of conclusions would be premature.

l. Removal of ammonia by scrubbing with solutions.—A problem of considerable importance in the Haber process is that of removing from the gas the ammonia which has been synthesized by passage through the catalyst. At Sheffield it was planned to do this by refrigeration. In Germany it has been done by water scrubbing.

The laboratory has investigated the removal of ammonia by scrubbing the mixed gases with solutions which will have a lower vapor pressure than pure water. The effort was made to find a scrubbing solution that would not introduce into the gas system any substance deleterious to the efficiency of the catalyst, that would have a high absorptive power for ammonia, readily give up the ammonia again, and not be corrosive to ordinary iron and steel. Several solutions of this type have been found and a study has been made of the vapor pressures of their solutions with ammonia and varying amounts of salts and water present.

From the results thus far obtained the most satisfactory solutions tested are lithium nitrate, calcium nitrate, and sodium iodide. Solutions of these substances as scrubbing agents possess the advantage over water of not leaving more than a slight trace of moisture in the scrubbed gas which is returned to the catalyst chamber.

Lithium nitrate solution seems most satisfactory of the three substances named, and by employing it so that absorption or scrubbing takes place around 10° C. and recovery of the ammonia from the lithium solution is accomplished at 40° C., the ammonia may be obtained free from other materials and can be collected as liquid or neutralized by acids to form ammonium salts.

More detailed results along this line will be found in the July, 1921, number of the Journal of the American Chemical Society.

m. Removal of ammonia by solid absorbents.—In addition to the removal of ammonia by scrubbing, the removal by absorption in solids has been investigated. The absorption efficiencies of four solids were studied by passing a mixture of hydrogen and nitrogen gases containing about 6 per cent of ammonia through the solid at different rates of flow and at 100 atmospheres pressure until the gases leaving the absorption chamber carried about 1 per cent of ammonia. The temperature of absorption was that of the room in most cases, and recovery was effected both by heating and by evacuation of the absorption chamber.

The solids tested were gas-mask charcoal of a medium grade, silica gel, ultra-clay, and alumina gel. The efficiency was found to be greatest for the charcoal and somewhat less for the other materials in the order named. The high absorption of ammonia by one or two of these materials indicates the possibility of their use for concentration of the ammonia, and its direct liquefaction, or as an adjunct to the refrigeration method for recovery of ammonia. By employing a series of absorption chambers which could be used in rotation, the gases may be returned to the catalyst chamber freed from all their ammonia. It is expected that details of these results will be published in the Journal of the American Chemical Society.

n. Steel tests.—The problem of obtaining a material suitable for the construction of the converters or catalyst chambers in which the reaction between nitrogen and hydrogen to form ammonia is to take place is one of great importance and considerable complexity. Ordinary carbon steel can not be employed, since it is attacked by ammonia at high temperatures to form nitride of iron, and rapidly deteriorates, becoming porous, and in many cases so brittle that it can be broken with the fingers.

The converters at Sheffield were constructed from chrome-vanadium steel, and that material has been used in our own testing bombs with considerable success.

In order to obtain really reliable information in this field, the laboratory has constructed a furnace containing 25 bombs made from different materials. Each bomb contains two bars for tensile tests, two specimens for impact tests, and one piece for corrosion tests.

The materials for the test bombs and specimens comprise 1 sample pure iron (Armco), 1 chromium steel, 1 vanadium steel, 7 chromium steels with varying additions of vanadium, 5 vanadium steels with varying additions of chromium, 1 tungsten steel, 1 uranium steel, 1 molybdenum chrome steel, 1 Monel metal, and 1 nickel. Several of the steels have been given different heat treatments, making 25 bombs in all.

Besides the main furnace there is an auxiliary furnace containing corrosion specimens to be removed at six successive intervals of time for determining rate of penetration.

The preliminary tests and micrographic examination of all the materials has been completed, and the actual test, which will last for six months to a year, according to the rate of deterioration, is about to start. The test bombs and specimens will be maintained at 500°, with 3 to 1 H_2–N_2 gas containing 8.5 per cent ammonia at 100 atmospheres pressure. It is expected that the final results of the test will be made available to the public.

o. Miscellaneous mechanical investigations.—In connection with the redesign of plant No. 1, a number of mechanical investigations have been carried out by Plant 1 Section of the Nitrate Division, working partially in cooperation with the Fixed Nitrogen Research Laboratory. The investigations have included:

Tests on several alloy steels to determine their properties at high temperatures: The properties tested were tensile strength, proportional limit, elongation, reduction of area, and strength at fracture throughout the range of 20° to 550° C. for four steels each containing 0.38 carbon and as follows: (*a*) Plain carbon, (*b*) 3½ per cent nickel, (*c*) 3 per cent nickel, 1 per cent chromium, (*d*) 1 per cent chromium, 0.2 per cent vanadium. While the report on file in the nitrate division gives full details of these tests, it may here be mentioned that the chrome-vanadium steel appeared to have the most desirable qualities for ammonia bombs, but even this steel for operation at 500° C. requires a factor of safety double that allowed at normal temperature.

Tests of devices for control of liquid levels in vessels operating at high pressures: Many mechanical and electrical devices were considered and rejected. A device tested and found satisfactory consists of a special sheathed resistor, partially or wholly immersed in the liquid whose level is to be controlled. The terminals pass out of the vessel through specially packed electrical terminals and connect to a source of current in whose circuit is a series motor whose torque will vary as the current through the resistor varies but whose rotation is opposed and limited to a small arc by a second motor of like capacity and attached to the shaft of the first motor. The torque is applied to move a lever which controls an oil-operated piston valve which in turn controls the rate of flow of liquid from the vessel. This mechanism was thoroughly tested and gave satisfactory results.

Tests of gaskets to withstand high gas pressures: Thorough study was made to determine a satisfactory gasket material and shape to hold gases at high pressure in vessels whose temperatures may vary and consequently cause both lateral and vertical differential expansions and contractions. Finally, laminated copper, in tongue and groove joints, was determined on and extensively tested on the compression machines at the Bureau of Standards. These tests did not, of course, subject the gaskets to gas loads, but the action was sufficient to indicate that such a type joint could be utilized satisfactorily on large vessels as well as on small ones, as has actually been done at the Fixed Nitrogen Research Laboratory.

Tests of high-pressure packed electrical terminals: After tests had been made on various methods and means for carrying electrical leads through the walls of high-pressure vessels, there was chosen the stuffing box type which utilized a soapstone packing. The soapstone not only insulates the lead from the vessel but holds the gas pressure very well, even at high temperatures.

Tests on 3½ inch high-pressure valves: Several different types of valves were designed to operate against hydrogen and nitrogen at high pressure and temperature and two of them built and tested. The final design has several novel features, more particularly the spring mechanism which takes up differential expansions and contractions. Very many types of packing were tested with these valves before a type was found which could be considered satisfactory to operate against gas at high temperature and pressure.

Test was made to determine the friction of flow of gases at various velocities over various depths of ammonia catalyst: This test was made to determine whether gases could be passed, either up or down through catalyst and whether or not there might be a small limit to the depth through which gas might be passed through a catalyst before the friction of flow would become excessive.

A special packed heat interchanger was tested: Although the data obtained did not give sufficiently consistent results to enable mathematical conclusions, they were all indicative of the fact that an interchanger of the design used would give an efficiency several times as great as the ordinary tubular type can give.

Test of special Klinger type sight gauge made at the Fixed Nitrogen Research Laboratory proved that sight gauges could be constructed to operate safely and satisfactorily on gases at 100 atmospheres pressure. These gauges are essential at many points in an ammonia process, and the standard Klinger gauge would not hold.

A design of differential pressure gauge was constructed, but under test failed because the magnetic operation of the gauge needle failed to give the results expected. Other preliminary designs have not yet been tested.

There was designed and tested a new type needle valve: This valve is in satisfactory operation in the catalyst plant of the Fixed Nitrogen Research Laboratory.

In considering electrolytic hydrogen for the direct synthetic process it was found that cells much larger than those now built would be necessary. The Electrolabs Co. of Pittsburgh constructed a 10,000-ampere cell, partially at Government expense, and with members of the Nitrate Division and of the Fixed Nitrogen Research Laboratory, subjected it to extensive test, which proved that cells of that capacity were feasible of construction and economical of operation.

Other miscellaneous tests, including determination of corrosion by ammonia on various metals and practicability of special stuffing boxes, were conducted.

2. The Cyanamide Process.

In connection with the cyanamide process the work of the laboratory has been largely determined by the governmental possession of United States Nitrate Plant No. 2 at Muscle Shoals, Ala. This plant is designed to produce as its final product 110,000 tons of ammonium nitrate per annum, to be used in explosives. In order to utilize this plant in peace times it is evident that the fixed nitrogen which it can produce must largely go into fertilizers, since there is no other use for fixed nitrogen of sufficient magnitude to absorb the tonnage involved. Hence the most important work which the laboratory has had to carry out in connection with the Muscle Shoals plant has been to consider what products having fertilizer value could be made at Muscle Shoals. This work will be discussed below in a section on "The Properties and Methods of Transforming Nitrogen Products" and a section on "Agricultural Experiments." In the present section we shall merely discuss the experiments which have been made on the cyanamide process itself. These have been relatively few in number, since the cyanamide process is rather thoroughly established and presents less opportunity for improvement than others.

a. Utilization of lime fines.—About 25 per cent of the limestone burned at Muscle Shoals finally comes through in the form of lime fines, which can not be utilized for the manufacture of carbide. For this reason the laboratory has considered the possibility of briquetting this material for use in the carbide furnaces. It has been found possible by using a roll press and coal-tar pitch as a binder to produce briquets of sufficient strength for this purpose at a cost of about $3.25 per ton. A large part of this cost is that for the binder, and further research would be necessary to make certain whether such briquetting might be made economical.

b. Study of the fundamental reaction of the cyanamide process.—The laboratory has initiated an investigation of the fundamental reaction between carbide and nitrogen by which nitrogen is fixed in the cyanamide process. This reaction may be written:

$$CaC_2+N_2=CaCN_2+C.$$

The heat of the above reaction has been measured at 25° by the combustion of carbide in nitrogen in a bomb calorimeter. The heat of formation of 1 mol of $CaCN_2$ from CaC_2 and N_2 at 25° was found to be 97,800 cals. By a different method, i. e., combustion of pure $CaCN_2$ in oxygen, N. Kameyama[1] has obtained a lower value, but this is based on a value for the heat of formation of calcium carbide concerning which there is considerable doubt.

In order to calculate with certainty the heat of the reaction at 1,000° C., i. e., the lowest temperature at which it can be calculated from equilibrium measurements, the specific heats of calcium carbide and cyanamide have been measured between 25° C. and 1,000° C. These measurements result in a calculated value for the change in the heat of the reaction per degree centigrade of —3.2 cal. between 25° and 1,000° C. The heat of reaction thus becomes 95,300 cals. per mol at 1,000° C.

Measurements have also been made of the equilibrium pressure of nitrogen over mixtures of carbide, cyanamide, and carbon at varying temperatures. These measurements have been carried out by exposing boats of carbide to nitrogen at different pressures and temperatures in a tube furnace and then withdrawing the boat and analyzing for the cyanamide found.

Plotting the pressure at which complete nitrification is obtained against temperature, preliminary experiments with 60 per cent carbide resulted in a pressure-temperature curve between 1,000° and 1,300°, which extrapolates to one atmosphere at 1,366°. The experiments were then repeated with a higher grade (83 per cent) carbide and with more accurate temperature control. The resulting pressure-temperature curve gave substantially higher temperature values for the same pressures, extrapolating to one atmosphere at 1,490° C.

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[1] J. Coll. Eng. Tokyo Imp. Univ. 10: 249–63 (1920), C. A. 15: 1110 (1921).

This change is in agreement with that predicted by Caro.[2] The reaction heat calculated from this pressure-temperature curve by using the simple Clausius equation was found to be about 66,000 cals. at 1,000° C. instead of 95,300 cals., calorimetrically measured. However, the pressure of the gas phase was found to be dependent on the concentration of nitrogen in the solid phase as well as upon the temperature, though less so at the lowest temperature of the experiments (1,000° C.) than at higher temperatures. Such a result can best be explained by the fact that the system is not a monovariant one, i. e., the equilibrium constant depends not only on the pressure of the gas phase but also on the composition of one or more solid phases, which explanation is in agreement with the conclusion of Le Blanc and Eschman.[3] Under these circumstances an agreement between the measured heat of reaction and that calculated from the simple Clausius equation is not to be expected.

c. Catalyst for the reaction $CaC_2+N_2=CaCN_2+C$.—Preliminary experiments on catalysts for the nitrification of carbide have been made employing a 60 per cent carbide and various salts, especially the halides of the alkali and alkaline earth metals, and curves have been obtained expressing the rate of nitrification in the presence of from 2 to 10 per cent of the catalyst. Satisfactory duplication of results has been difficult to obtain, and consequently a study of various methods has been undertaken, an investigation of which is still under way.

d. Disposal of autoclave sludge.—A serious problem arises in the production of ammonia from cyanamide because of the large amount of autoclave sludge produced. It is possible that this material could be used to advantage for its agricultural value owing to its lime content. Up to date, however, no methods for its disposal outside of flowing it out into a settling pool or lake have been suggested.

This laboratory has considered the possibility of recovering the graphite in this material, but has not yet been able to find any purely mechanical or electrical method of separating the graphite from its intimate combination with the lime. Furthermore, it is to be noted that even if such separation could be effected, the material obtained would be a relatively low-grade powdered graphite rather than the valuable flake graphite. The material might, however, be good enough for the manufacture of electrodes for the carbide furnaces.

By chemical means it has been found that the graphite can be recovered. Thus, by treating the sludge with nitric acid it is possible to produce calcium nitrate and graphite. This possibility has, however, little to commend it, since calcium nitrate is not a standard product in this country and the operation of the plant would be very unbalanced under these conditions.

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[2] Zeit. für angew Chemie (1909), p. 1178.

[3] Zeit. für Elektrochemie, 17 : 20–34 (1914).

3. The Arc Process.

Since the Government has no plant designed to operate in accordance with the arc process, research at the laboratory along the lines of the arc process has been limited to a fundamental study of the nature of electric discharges in gases and the way in which they produce chemical reactions. Two pieces of work of this kind have been completed and are briefly described below.

a. Nature of corona discharge as shown by motion of particles.—The corona discharge in air at atmospheric pressure between a central wire and flat plates has been investigated by photographing the motion of particles of various kinds which are introduced into the field. These particles were found to move either toward the plate or the wire, in accordance with the charge they receive, which may come from ions in the corona field, from contact with the central wire, electrostatic induction, or leak from the earth. The results showed that the corona field outside of a small ionizing region is filled with ions of the same sign as the central wire, and in the case of alternating currents these ions follow very closely the change in the polarity of the central wire. The results are of some importance in explaining the behavior of Cottrell precipitators and in giving a picture of the corona field. This work is described in more detail in Chem. and Met. Eng. 22; June 30 (1920).

b. Yield of ozone in corona discharge.—As a typical reaction taking place in the electric discharge, the laboratory has studied the yield of ozone in the corona discharge both in glass ozonizers and in discharge tubes provided with a central wire. In the case of glass ozonizers it was found that the yield of ozone per kilowatt hour decreased with increasing frequency, the rate of energy input and other variables being held constant. This decrease in yield with frequency, in the glass ozonizers, was found to be largely, if not completely, due to the increasing loss in the dielectric· In the case of all metal ozonizers, it was found that the yield was practically independent of the frequency. This is contrary to the general impression, which has been that higher yields could be obtained with higher frequencies. This error has perhaps been due to the fact that with glass ozonizers more alternating current can, of course, be made to flow through the apparatus with the same voltage at higher frequencies, and hence the total yield obtainable for a given apparatus is increased, although the yield per kilowatt hour is lowered when the frequency is raised.

It is hoped that further details of this work will be published in the near future.

4. The Cyanide Process.

Although numerous attempts have been made to operate cyanide processes for the production of ammonia, the costs have always been excessive, and it is now evident that cyanide processes on the order of these past trials can never compete with established processes such as the cyanamide or Haber processes.

The only hope that the cyanide process may ever be successful lies in research of two types.

In the first place it is imperative that we have a more accurate knowledge of the fundamental reactions involved in the formation of sodium cyanide. No careful study of these reactions has ever been made, though many partial but unsubstantiated theories have been offered. As a consequence the yields obtained and the rates of formation of cyanide have been erratic and uniformly lower than expected.

In the second place there is need for what might be termed "engineering research." That is to say, the prospects for a successful process would be greatly improved if a more satisfactory means of manipulating the charge under treatment could be devised. In fact, no possible chemical improvement could make the process successful unless the mechanical methods of handling can also be improved. The principal difficulties have arisen from the necessity of heating the charge out of contact with flame. As always carried out heretofore, the charge has been, at the reaction temperature, a solid or semisolid mass of small briquets. This type of material has a very low heat conductivity, and the thermal efficiency of the process has therefore been extremely low. Further disadvantages of this type of heating are the rapid burning out of the metallic retorts in which the charge is treated, and the small capacity of the retorts with consequent high labor costs.

Work on the first type of research has been started at the Fixed Nitrogen Research Laboratory. It is already apparent that the reaction is not nearly so rapid as has been sometimes claimed. Moreover, the results are erratic and the conversion not high, results above 50 to 60 per cent conversion being unusual. It has also been found that care must be used in selecting the coke used for the briquets. Certain commercial grades of coke containing considerable silica and alumina give practically no conversion.

It is hoped that ultimately an exhaustive study of the mechanism of the process will be completed, including a determination of the intermediate reactions which take place, the speed of these intermediate reactions, the factors governing the speed of the intermediate reactions, and the factors determining the maximum conversion of sodium carbonate to sodium cyanide.

No research of an engineering type is yet being carried out by the laboratory, but it is hoped that a better insight into the nature of the reactions taking place may suggest new and better ways of carrying out the reactions on a large scale.

5. The Properties and Methods of Transforming Nitrogen Products.

A large part of the effort of the Fixed Nitrogen Research Laboratory has been devoted to a study of the transformation of nitrogen containing substances from one form to another. This has been of special importance in connection with the possible utilization of the Muscle Shoals plant, since the two products, cyanamide and ammonium nitrate, which the plant is designed to produce, are not now used in America in great quantities in peace times. The general conclusion has been reached that the peace-time operation of the Muscle Shoals plant is entirely feasible if changes in the plant are made. It is believed that such utilization is for the best interests of the country, both from the point of view of agriculture and from the point of view of military preparedness, and that the operation of this plant for the manufacture of fertilizer and other substances useful in the arts can be made entirely self-supporting, and perhaps profitable if the interest charges on the capital invested are not made too high.

A brief statement of the results obtained by the laboratory with various transformation processes is given below:

a. Oiling and hydrating cyanamide.—The fundamental step in the cyanamide process consists in the reaction between calcium carbide and nitrogen to form calcium cyanamide. The crude product thus obtained goes by the name of lime-nitrogen and contains about 60 per cent calcium cyanamide, 18 per cent free lime, 12 per cent carbon, and 1.5 per cent carbide. Before this material can be autoclaved to form ammonia it is hydrated with enough water to destroy the carbide. This is called minimum hydration.

For use as a fertilizer material the addition of water to lime-nitrogen is carried beyond the point of minimum hydration in order to hydrate the free lime as well as destroy the carbide, and oil is also added to decrease dustiness, the completely hydrated and oiled material going by the trade name of Cyanamid. Since but little information is available in the literature concerning the best method of such oiling and hydrating operations, an investigation of this matter has been made at the laboratory.

It was found that considerable care must be taken in the oiling and hydrating operation to prevent the formation of undue amounts of the agriculturally undesirable substance dicyanodiamide.

Using a Werner and Pfleiderer jacketed mixer with a mixing chamber of about 1.9 cubic feet, dicyanodiamide was found to form in appreciable quantities if the conditions were as follows: A hydrator jacket at 80° C., a mixing time at this temperature of 60 minutes or longer, slow speed stirring (60 revolutions per minute at drive shaft), and an excess of water introduced as a coarse spray (5 openings one-sixteenth inch in diameter).

To prevent the formation of this material, the water must be added in a reasonably fine spray, with thorough agitation. Addition of more water than that theoretically required (6 to 6.5 per cent) should be avoided and the temperature should be as low as possible.

It was found that the loss of ammonia during hydration was negligible in spite of the strong odor (loss estimated as about 0.04 per cent of the total nitrogen present).

The increase in volume on hydration was found to be about 9 per cent.

The oil as well as the water should be introduced as a fine spray in order to insure proper distribution.

b. Granulation of cyanamide.—The dustiness of cyanamide and its toxicity to the human skin would make a granulated product very desirable. For this reason the laboratory has made studies of the possibility of granulating cyanamide by the addition of water and various aqueous solutions, followed by extrusion under pressure through a perforated plate. In agreement with the work of other investigators it has been found possible in this way to produce firm granules of entirely desirable physical characteristics. It was not possible, however, with such a granulation process to prevent the formation of excessive quantities of dicyanodiamide, which always arises when excess of water is added to lime-nitrogen. For this reason it seems doubtful if granulation with water can ever be successful when cyanamide is to be used for agricultural purposes.

Some experiments have also been made to see if the original lime-nitrogen pig could be crushed to desired size and the carbide then destroyed without disturbing the strength and size of the granules. This has, however, not been found to be feasible.

c. Treatment of cyanamide with sulphuric acid.—Cyanamide is a highly basic material, both because of the lime present and because of the basic nature of calcium cyanamide itself. For this reason its use in America in mixed fertilizers has been limited to about 50 to 60 pounds to the ton, since in large quantities its reaction with acid phosphate causes reversion of the phosphate to an insoluble form.

In order to overcome this difficulty, the laboratory has attempted the treatment of lime-nitrogen with enough excess sulphuric acid to insure the conversion of the cyanamide to the agriculturally desirable substance urea, followed by neutralization of the excess acid with ground phosphate rock to produce soluble phosphate.

It was not found possible, however, to make such a process entirely successful. A considerable amount of the nitrogen is converted, instead of to urea, into the agriculturally less desirable substance, guanylurea. Some of the nitrogen also goes to ammonia, which decreases the amount of excess sulphuric acid available for action on the phosphate rock. And, finally, the phosphate rock which has to be added can be only partially converted to the soluble form.

Controlling the temperature by blowing air through the reacting mass, it was found possible to produce a material which contained about 6 per cent total P_2O_5 and 6 per cent nitrogen. About 50 per cent of the P_2O_5 was in the citrate-soluble form, and the nitrogen was present in the following forms: Urea, 55 per cent; guanylurea sulphate, 33 per cent; ammonium sulphate, 5 per cent; undetermined, 7 per cent.

The physical quality of this material was entirely satisfactory. Its chemical nature, however, can not be regarded as satisfactory. Furthermore, cost estimates indicate that the contained nitrogen and phosphate would be more expensive than in equivalent amounts of ammonium sulphate and acid phosphate.

d. Calcined phosphate for mixture with cyanamide.—Owing to the impracticability of using large quantities of cyanamide in a fertilizer containing acid phosphate, the suggestion has often been made that cyanamide might be mixed with a new material known as calcined phosphate, which may be made by heating phosphate rock together with niter cake and carbonaceous material in a rotary kiln. This calcined phosphate can be made so as to contain a high percentage of citrate soluble phosphate, and its mixture with cyanamide has been found to be entirely feasible.

The new material, calcined phosphate, has not yet come on the market, although a new company, the Midwest Chemical Co., has recently been formed at Nashville, Tenn., to undertake its manufacture.

In order to assist in obtaining information which might be valuable in the manufacture of calcined phosphate, the laboratory has carried out a very considerable number of experiments on the production of this material, using a Fletcher gas furnace as well as a 3-foot rotary kiln. Using ground phosphate rock and any alkali, or an alkaline salt, together with enough carbon to reduce it, it was found possible to obtain by calcination a material having a high citrate solubility. The general conclusion was reached that the calcination process is technically feasible and that citrate soluble phosphate could probably be produced by this process at a lower cost than by the manufacture of acid phosphate.

The chemical nature of the changes produced in the phosphatic material was found to be very complicated, and it is believed that at least part of the increase in solubility is due to an increase in the fineness of subdivision of the tertiary calcium phosphate, brought about by an intermediate reaction between the calcium phosphate and the alkaline oxide during the calcination followed by regeneration of the calcium phosphate in a lower part of the kiln.

e. Storage experiments on mixtures containing cyanamide.—The changes that occur on storage in mixtures of fertilizer materials that contain cyanamide are a matter of great importance from the agricultural point of view. The worst thing that can happen on storage of such mixtures is the formation of dicyanodiamide. This material is not only somewhat toxic to plant growth but is even more harmful in killing or preventing the action of the nitrification bacteria in the soil, and thus delays the transformation of ammonia nitrogen into nitrate nitrogen. Another undesirable reaction that can take place in fertilizers containing both cyanamide and acid phosphate is the reversion of the phosphate to the citrate insoluble form. This reaction occurs because of the free line in cyanamide and also because of the highly basic character of calcium cyanamide itself and has limited to small amounts the addition of cyanamide to fertilizers containing acid phosphate.

Work in the laboratory has shown that cyanamide can be mixed with calcined phosphate or with the duplex basic phosphate manufactured by the Tennessee Coal & Iron Co. without any appreciable reaction taking place between the cyanamide and the phosphate, even on continued storage.

When mixed with acid phosphate in the proportion of 50 pounds of cyanamide to a ton of mixed fertilizer containing 1,000 pounds of acid phosphate and the balance inert material, it is found that the cyanamide is largely converted into urea. When the proportion is raised to 100 pounds to the ton, prohibitive amounts of dicyanodiamide are formed within a few days. This formation of dicyanodiamide coupled with the reversion of acid phosphate means that large additions of cyanamide to mixed fertilizers must be made very cautiously.

In connection with the results just described it should be noted that these experiments were made using cyanamide and acid phosphate in the proportion of 50 pounds to 1,000 pounds, and inert material to represent the remainder of the ton. In actual fertilizer practice the formation of dicyanodiamide may be greatly lessened by the interaction of cyanamide and organic forms of nitrogen present in the mixture coming from tankage or other similar material. Under these conditions it is believed that with proper control greater amounts than 50 pounds of cyanamide to the ton might prove to be practicable.

In connection with the use of cyanamide it should be pointed out that mixture with chlorides should be avoided, owing to the formation of the very hygroscopic salt calcium chloride. This may lead to the absorption of considerable water, which itself produces favorable conditions for the reaction of cyanamide to form dicyanodiamide.

f. The chemistry of cyanamide.—A thorough knowledge of the chemical behavior of cyanamide in aqueous solutions is of great importance both from the point of view of the utilization of cyanamide as a fertilizer and also from the point of view of using cyanamide as a basic material for the synthesis of organic compounds. The laboratory has carried out rather extensive research on this matter which it is hoped may be published in the near future. A few of the significant results may be stated here.

Free cyanamide is a very weak acid and in neutral solutions is largely present as the undissociated acid H_2CN_2 and this substance is relatively stable in neutral solution.

The addition of acid to a neutral solution of cyanamide leads to hydrolysis to form urea in accordance with the reaction.

$$H_2CN_2+H_2O=(NH_2)_2CO.$$

This reaction has been found to be of the first order, the velocity constant being approximately proportional to the concentration of hydrogen ion, which acts as a catalyst. Practically complete conversion to urea can be obtained in this manner.

The addition of an alkali to a solution of free cyanamide also leads to hydrolysis to form urea, hydroxide ion as well as hydrogen ion apparently being a catalyst for the reaction. The addition of an alkali has, however, an additional effect in leading at the same time to the polymerization of cyanamide to form dicyanodiamide. The experiments of the laboratory in this connection have led to a substantiation of the ionic theory of Grübe and Nitsche for the formation of dicyanodiamide. The first effect of alkali addition is to lead to the formation of the acid cyanamide ion in accordance with the reaction

$$H_2CN_2+\overline{OH}=H_2O+H\overline{CN}_2.$$

The acid ion and the remaining free cyanamide then react to form the negative ion of dicyanodiamide in accordance with the reaction

$$H\overline{CN}_2+H_2CN_2=\overline{H}_3C_2N_4.$$

In particular justification for these ideas it has been found that although the rate of hydrolysis of cyanamide to form urea increases continuously with additions of alkali, the rate of dicyanodiamide formation passes through a maximum when the alkali addition is such as to give an approximate equality of the free cyanamide and acid cyanamide ion present.

These results have been found of great value in interpreting the behavior of aqueous extracts from cyanamide, in interpreting the behavior of fertilizer mixtures containing cyanamide, and in developing methods for the preparation of free cyanamide, dicyanodiamide, etc.

g. The preparation of cyanamide.—The substance free cyanamide H_2CN_2 is an important one from the research point of view and as a base for organic syntheses. If it could be made with reasonable cheapness from cyanamide, its use might be greatly extended.

The usual methods for the preparation of this material have been very complicated, expensive, and practicable only on a laboratory scale. They have consisted, in general, of the following steps: (1) Liberation of free cyanamide by treatment of cyanamide with an acid in the presence of the entire lime content, keeping the temperature as low as possible, (2) drying the cyanamide-acid slurry as rapidly as possible and yet at a comparatively low temperature, about 40° C., (3) extraction of the free cyanamide from the dried slurry by means of ether, followed by concentration of the ether solution and recrystallization, if desired.

These methods always lead to the formation of considerable dicyanodiamide and urea during the neutralization process and there is a large waste of the expensive material, ether.

The laboratory has developed an efficient method for the production of this material which is based on the stability found for free cyanamide in strictly neutral aqueous solutions. The following process has been found to be satisfactory.

Extract cyanamide with five times its weight of water at a temperature not exceeding 25° C. Through agitation of the slurry for two hours is sufficient to give as good as 94 per cent extraction.

The solution thus obtained is found to contain calcium acid cyanamide Ca $(HCN_2)_2$. It is separated from the sludge in a filter press, and washed with an amount of water about equal to the original weight of cyanamide.

The solution is then *exactly* neutralized with sulphuric acid and the precipitated calcium sulphate filtered and washed.

The *neutral* solution thus obtained can be safely evaporated at 75° C. and crude cyanamide H_2CN_2 be obtained with a purity of over 90 per cent. The total yield by this method is also better than 90 per cent. Repurification from ether can be used if a purer product is desired.

h. The preparation of dicyanodiamide.—Experiments have been made at this laboratory to determine the best methods of producing dicyanodiamide. The following process has been found to be satisfactory.

Extract cyanamide for 30 minutes with five times its weight of water at a temperature between 45 and 50° C.

Filter the slurry as quickly as possible, washing with an amount of water about equal to the original weight of the cyanamide.

Add at once enough sulphuric acid to put half the cyanamide in the free form, thus obtaining the best conditions for polymerization. Raise the temperature to 75° and gradually add the remaining acid necessary for complete neutralization. This addition should keep pace, of course, with the process of polymerization, which will take in all about two hours at 75° C.

Filter off the calcium sulphate and recover the dicyanodiamide from solution by evaporation and recrystallization, if desired. The first crystallization should give a product 90 to 94 per cent dicyanodiamide and a single recrystallization 96 to 97 per cent dicyanodiamide. The total recovery should be about 85 per cent dicyanodiamide. About 10 per cent of the nitrogen goes to urea and the rest into undetermined substances.

i. The preparation of guanidine.—Owing to the present interest in nitroguanidine as a possible constituent of smokeless powders, the fact that cyanamide is the natural commercial source for guanidine becomes a matter of considerable significance. Guanidine itself and other derivatives thereof are also liable to be of commercial importance in the future.

The laboratory has found that guanidine salts can be most advantageously prepared by autoclaving at 155° a solution containing free cyanamide, prepared as described above, and the corresponding ammonium salt. In the case of guanidine nitrate a yield of about 80 per cent figured on the basis of the cyanamide can be obtained.

j. The production of urea from ammonia and carbon dioxide.—One of the most attractive nitrogen-containing materials from a fertilizer standpoint would be the substance urea, if it could be manufactured cheaply enough. At the present time this material is generally regarded as a chemical to be sold in small lots with prices of over a dollar a pound. Considerable quantities, however, go into the manufacture of transparent celluloid, such as is used in moving-picture films, and although this is not sold in the open market, it undoubtedly moves at considerably lower prices.

For the larger quantities needed in the celluloid industry, urea may be produced from cyanamide by acid hydrolysis or may be manufactured from ammonia and carbon dioxide by a method which is apparently already in operation in Germany.

The ammonia-carbon dioxide method is undoubtedly the most hopeful one for the future. The process consists in the preparation of ammonium carbamate by condensation from ammonia and carbon dioxide gases, followed by autoclaving at a temperature over 100°, thus obtaining a partial conversion into urea in accordance with the reaction

$$(NH_3)_2CO_2=(NH_2)_2CO+H_2O.$$

The unconverted carbamate is then distilled off from the urea and put through the process once more with the addition of enough ammonia and carbon dioxide to make up the original mixture.

The laboratory has experimented with this process and determined the best methods for carrying out a number of the steps. It has been found that autoclaving at 150° C. will lead to a 40 per cent conversion to urea in four hours. Methods for the condensation of carbamate in a condenser provided with a rotary scraper have been developed, and the practice of briquetting the carbamate so that it can be loaded into the autoclave without the necessity of cooling down has also been investigated. Patents covering these features have been applied for.

There seems a possibility that urea might ultimately be obtained at fertilizer prices by using the carbamate process, and in any case the production of urea for the celluloid trade by the carbamate method should be very attractive.

k. Decomposition of urea in sulphuric acid.—One of the important reactions of urea is its decomposition to form ammonia in accordance with the reaction

$$(NH_2)_2CO+2H_2O=2\overset{+}{NH_4}+\overset{-}{CO_3}.$$

It is generally believed that this reaction is catalyzed by the presence of hydrogen ion, and work in this laboratory has confirmed this point of view. Work in this laborary has also shown, however, that very large additions of acid decrease the rate of decomposition. This may be explained by the formation of a salt of urea in concentrated acid which protects it from decomposition.

l. Ammoniated superphosphate.—A possible method of putting large quantities of ammonia into a form available for fertilizer purposes would be to absorb the ammonia in acid phosphate and thus produce a material containing both phosphate and ammonia.

Experiments made on this material at the laboratory have shown that ammoniated superphosphate containing 5.5 to 6 per cent ammonia can be made, using ordinary 16 per cent superphosphate. The final product contains approximately the same per cent total phosphoric acid as the original superphosphate, owing to elimination of water. About 80 to 85 per cent of this phosphate is soluble in 2 per cent citric acid, but the solubility in ammonium citrate is considerably reduced. The conclusion was reached that this would be a profitable material to manufacture if it could be sold on the basis of its citric acid solubility, but that it would not compete with equivalent quantities of ammonium sulphate and superphosphate if it had to be sold on the basis of the citrate solubility of its phosphoric acid.

m. Ammonium phosphate.—The production of monoammonium phosphate would be an ideal way of disposing of ammonia if phosphoric acid could be produced at a low enough figure. At the present time phosphoric acid is produced by the American Cyanamid Co. by treating phosphate rock with sulphuric acid. This acid is then neutralized with ammonia, the resulting material sold under the trade name of "Ammo-Phos." This process, however, requires for the manufacture of a given amount of ammonium phosphate more sulphuric acid than the equivalent amount of acid phosphate and ammonium sulphate, and hence can not compete except where high freight rates give an advantage because of the highly concentrated nature of the final product. For this reason "Ammo-Phos" has only been manufactured for the export trade.

The production of cheap phosphoric acid directly from phosphate rock by a thermal or electrothermal process would be a great advance and one which is fairly certain to occur within the next decade. This material is already being produced in the electric furnace on a commercial scale by the Federal Phosphorus Co., of Anniston, Ala. In this connection a considerable number of experiments have been carried out at the laboratory to determine the mechanism of the chemical reactions by which phosphorus is liberated from phosphate rock. The following somewhat tentative conclusions have been reached:

(*a*) P_2O_5 can not be expelled from $Ca_3(PO_4)_2$ by silica below 1,800° C. to 2,000° C. The reason for this is the stability of $Ca_3(PO_4)_2$ as against the very weakly acidic character of Sio_2.

(*b*) $Ca_3(PO_4)_2$ is reduced by carbon, the reaction beginning about 1,300° C. Up to 1,500° phosphorus is liberated, leaving a residue of lime, CaO. At 1,700° to 1,800° a mixture of calcium carbide and calcium phosphide is formed.

(*c*) The mechanism of the reaction of calcium phosphate, silica, and carbon is believed to be partly in accordance with the following equations:

$$Ca_3(PO_4)_2+3SiO_2=Ca_3(PO_4)_2.3SiO_2$$
$$Ca_3(PO_4)_2.3SiO_2+5C=3CaSiO_3+2P+5CO$$

A portion of phosphorus is probably also liberated according to the equations:

$$Ca_3(PO_4)_2+5C=3CaO+2P+5CO$$
$$CaO+SiO_2=CaSiO_3.$$

The reaction of calcium phosphate, silica, and excess carbon occurs quite rapidly even at 1,300°, incipient clinkering taking place at about this temperature.

If phosphoric acid made by some thermal method does become available in large quantities, it will have the added advantage of greater concentration than that made by the sulphuric acid process. This will make it possible to produce ammonium phosphate in saturators similar to those used for ammonium sulphate manufacture, the precipitated salt being removed by centrifugation without the necessity of evaporation as is the case with dilute acid. The methods for carrying out such a process have been worked out in the laboratory and patented.

n. The graining and coating of ammonium nitrate.—The Muscle Shoals plant produces as its final product ammonium nitrate. This material was intended for use as a high explosive in mixture with T. N. T. to form the material known as amatol. Ammonium nitrate has not, however, been used for fertilizer purposes in more than experimental amounts, and in the untreated form is too deliquescent and too liable to cake to make such use feasible. For this reason, the laboratory has undertaken researches to determine the best methods of graining and coating this material so as to reduce its hygroscopicity and liability to cake.

Experiments on the graining of this material were carried out in a small graining kettle which reproduced the conditions actually obtained in the kettles used when ammonium nitrate is grained for the manufacture of high explosives.

It was found most desirable for fertilizer purposes to obtain large grains (20 mesh) with the least possible water content. Small grains have a larger relative surface which leads to increased hygroscopicity, and high-water content leads to a gradual process of solution and recrystallization with a consequent setting up or caking.

The grain size was found to be dependent on the melting point (i. e., water content) of the molten ammonium nitrate which is introduced into the graining kettle. A low water content with consequent high melting point leads to the production of large grains. Such a low water content also has, of course, the additional beneficial effect of reducing the moisture of the final product. A further means of reducing the water content of the final product was found to lie in a prolonged stirring of the material at the transition temperature of 125° where the ammonium nitrate undergoes a transition from the regular to the rhombohedral crystal form. This transition is accompanied by evolution of heat which together with the change in crystal form seems to produce ideal conditions for water expulsion.

For coating the grained material a number of substances were tried with the final conclusion that 2 per cent of petrolatum introduced into the graining kettle when the temperature has come down to 70° C. gives the best results.

The final material obtained by this graining and oiling process is more hygroscopic than Chilean saltpeter or ammonium sulphate. Nevertheless, it is believed that it could be satisfactorily used in mixed fertilizers.

o. The graining and coating of calcium nitrate.—Calcium nitrate, sometimes known as Norwegian saltpeter, is one of the common end products of the arc process. This material suffers from the same disadvantages for fertilizer use as ammonium nitrate and is perhaps even more hygroscopic.

For this reason the laboratory has initiated experiments on the graining and coating of calcium nitrate similar to those on ammonium nitrate, but the best conditions for doing this have not yet been fully determined.

p. Double salt of ammonium nitrate and ammonium sulphate.—Reports indicate that a double salt of ammonium nitrate and ammonium sulphate is being used for fertilizer purposes in Germany. Experiments with this material have been made at the laboratory.

The salt has the composition $(NH_4)_2.SO_4 2NH_4NO_3$ and hence would be a relatively concentrated fertilizer material. It can be prepared by crystallization from solution and centrifugation. It has been found desirable to control the conditions of preparation very carefully and to wash the centrifuged material with a saturated solution of ammonium sulphate. The material is less hygroscopic than ammonium nitrate and could probably be used in fertilizers. Its agricultural value has been found to be excellent.

Search for a double salt of ammonium nitrate and ammonium phosphate has also been undertaken at the laboratory, but none seems to exist.

q. Mixed salt from ammonium nitrate and potassium chloride.—As another method of putting ammonium nitrate in a satisfactory form for fertilizer use, it has been found possible to mix solutions of ammonium nitrate and potassium chloride and prepare by double decomposition a mixture of ammonium chloride and potassium nitrate in accordance with the reaction

$$NH_4NO_3 + KCl = NH_4Cl + KNO_3.$$

This mixed salt contains two fertilizer components, ammonia and potash, and the possibility of its manufacture would depend, of course, on obtaining for the potash a price at least as high as that originally paid for it. When made from reasonably high-grade potassium chloride the mixture is nonhygroscopic enough for fertilizer use.

r. Mixed salt from ammonium nitrate and potassium sulphate.—It has been found that a similar mixed salt to that just described can be made by the reaction

$$2NH_4NO_3+K_2SO_4=(NH_4)_2SO_4+2KNO_3.$$

This is also a technically satisfactory solution of the problem of putting ammonium nitrate in a form suitable for fertilizer use and has the agricultural advantage of introducing sulphate ion instead of chloride ion, which can not be used with some crops. To obtain a nonhygroscopic mixture, reasonably high-grade potassium sulphate must be used.

s. Ammonia oxidation to produce nitrogen tetroxide.—For military purposes fixed nitrogen in the nitrate form is necessary, and this has led to the development of methods for oxidizing the ammonia which can be obtained either from by-product coke ovens or from nitrogen fixation by the cyanamide or Haber processes. These methods consist in the passage of ammonia gas together with air through a catalyst, which is usually a hot platinum gauze. Oxidation takes place approximately in accordance with the reaction

$$4NH_3+5O_2=4NO+6H_2O.$$

Oxidation by such a method has been found to be quite satisfactory, although there is some loss of fixed nitrogen. The nitric oxide thus obtained is usually allowed to combine with excess oxygen to form nitrogen dioxide (NO_2) and is then absorbed in towers to give nitric acid as in the arc process.

The difficulty of shipping nitric acid leads to a consideration of the possibility of preparing liquid nitrogen dioxide (NO_2), or more strictly speaking, the polymer, nitrogen tetroxide (N_2O_4). This material could be shipped in cylinders and then used at the receiving point to produce nitric acid. Its direct use in the explosive anilite or as a nitrating or oxidizing agent for organic substances is also a promising possibility. For these reasons the methods of producing liquid tetroxide (N_2O_4) by the oxidation of ammonia have been considered by the laboratory.

The most difficult feature in such a production of liquid tetroxide lies in the fact that nitrogen dioxide and tetroxide react rapidly with water to form nitric acid, thus necessitating a rapid removal of most of the water produced by the oxidation.

It has been found that by rapidly chilling the gases which come from the oxidation chamber to 25° C., it is possible to condense out most of the water before the nitric oxide formed by the combustion has had time to react appreciably with the excess oxygen to form dioxide. Experiments have shown that the amount of fixed nitrogen taken up by the water thus condensed can be reduced to 0.4 per cent of the total.

After such a preliminary condensation of water, gases can be obtained containing about 12 per cent nitrogen dioxide and 3 per cent water vapor. By using air enriched with oxygen for burning the ammonia a higher percentage of the dioxide could be obtained. Experiments are now under way looking to the further separation from the 3 per cent water vapor, which will make it possible to obtain a pure dry liquid tetroxide suitable for shipment in cylinders.

t. Reaction between ozone and nitrogen tetroxide.—Studies have been made in the laboratory of the reaction between ozone and nitrogen tetroxide to form nitrogen pentoxide in accordance with the reaction

$$N_2O_4+O_3=N_2O_5+O_2.$$

Since this reaction forms the anhydride of nitric acid, it has some technical interest, owing to the possibility of using it for the preparation of fuming nitric acid of any desired concentration. The high cost of ozone manufacture would preclude its very general use, but it might be of importance in recovering dilute nitrous fumes leaving the absorption towers which would otherwise be wasted.

Experiments with the reaction have shown that with concentrations of ozone up to 7 per cent 1 mol of ozone is just enough to oxidize 1 mol of tetroxide. Experiments were also made with higher concentrations of ozone, but since ordinary analytic methods fail with ozone of high concentration, it has not yet been possible to determine whether or not the 1 to 1 ratio between the tetroxide and ozone is maintained.

The reaction between tetroxide and ozone was found to be practically instantaneous, a matter of interest from the technical point of view.

u. Decomposition of nitrogen pentoxide.—The rate of decomposition of gaseous nitrogen pentoxide has been studied by the laboratory.

In the dark the reaction was found to be monomolecular. The velocity constant was not affected by the introduction of glass wool into the reaction vessel, thus indicating a true monomolecular reaction rather than diffusion to the walls with subsequent reaction. The rate of reaction was determined at temperatures from 0° to 65° C. The temperature coefficient for the rate of reaction was found to be of the order of 300 per cent for a 10° rise. The critical increment for the reaction was found to be about 24,700 calories. On the basis of the Perrin-Lewis theory of reaction velocity, this would lead to a photochemical decomposition of nitrogen pentoxide by light of wave length of 1.16μ. A detailed description of the methods and results will be found in the Jour. Amer. Chem. Soc. 43: 53 (1921).

In the light the decomposition was found to be photochemical. It was found that light having wave lengths in the region 400 to 460μ accelerates the decomposition, provided the dioxide is present. In the absence of dioxide the photochemical action apparently ceases. Light of wave length 1.16μ was not photochemically active, in disagreement with the Perrin-Lewis theory of reaction velocity. A detailed description of this work will be found in the Jour. Amer. Chem. Soc. 43:72 (1921).

v. Vapor pressure of nitrogen pentoxide.—Measurements have been made at the laboratory of the vapor pressure of solid nitrogen pentoxide. They will be found in the Jour. Amer. Chem. Soc. 42:1131 (1920).

w. Methods of analysis for dicyanodiamide and urea.—In the work of the laboratory on cyanamide and its derivatives, methods of analysis for dicyanodiamide and for urea have been developed which have been largely responsible for the success achieved in following the complicated changes which take place when cyanamide is mixed with fertilizers or used as an aqueous extract. Previous to the development of these methods, urea under such circumstances has almost always been determined by difference, while the analysis for dicyanodiamide has been subject to great uncertainties, usually in the direction of too high results. A description of these methods will be of use to other investigators.

The method for the determination of dicyanodiamide is based on the fact that dicyanodiamide is converted quantitatively to guanylurea when heated with acid in water solution. The guanylurea is precipitated as nickel guanylurea and weighed as such. It has been necessary to do considerable research work on this method to determine the optimum conditions for the conversion and precipitation, as the length of time for digestion and the concentration of the acid largely determines the accuracy of the method.

A suitably sized sample of cyanamide is extracted with acetone for about three hours, filtered through a dry filter, and an aliquot of the filtrate taken just to dryness on the steam bath. The residue is taken up with 20 to 25 c. c. of N/4 HNO_3 and again taken to dryness in about two hours' time. This residue is taken up with about 15 c. c. of an ammoniacal 10 per cent mannitol solution saturated with nickel guanylurea. Addition is made of 1 to 2 c. c. of nickel nitrate solution (20 g. $Ni(NO_3)_2.6H_2O$—10 g. NH_4NO_3—60 c. c. H_2O, saturated with nickel guanylurea), followed by 20 per cent NaOH solution until the color changes to greenish yellow. The container is tightly covered and allowed to stand overnight. The precipitate is gathered in a weighed Gooch crucible, washed with about 100 c. c. of dilute ammonia water saturated with nickel guanylurea. The crucible is dried at 125° C. for one hour and again weighed.

The salts of guanylurea and biguanide are the only known derivatives of cyanamide that will interfere, and, as these substances are insoluble in acetone, they do not interfere in an acetone extraction. In case of water solutions, however, containing these compounds they must be either removed previous to digestion or else determined as a blank.

x. The determination of urea in cyanamide and cyanamide mixtures.—For urea a method has also been developed at this laboratory whereby urea can be easily and rapidly determined in cyanamide and cyanamide mixtures. The enzyme, urease, which converts urea into ammonium carbonate, is the reagent used. The procedure is a modification of the method recommended by Marshall[5] for the determination of urea in urine. A suitably sized sample is extracted with water for two hours, the calcium precipitated by the addition of anhydrous sodium carbonate, and the extract filtered through a dry filter. An aliquot of the filtrate is made distinctly acid with HCl, using methyl-red as indicator, and aerated five minutes to remove excess CO_2. It is then made exactly neutral and 10 c. c. of neutral urease solution added. After standing for one hour at room temperature, a measured excess of standard N/10 HCl solution is added, followed by a second aeration for five minutes. The excess acid is then titrated with standard N/10 NaOH solution. The acid used up is a direct measure of the ammonia formed from the urea.

In case phosphates are present, it is necessary to remove them also previous to the addition of the urease solution. This can be done by precipitating with $Ba(OH)_2$. The excess barium is then removed, together with the calcium, as carbonates.

The urease solution is best prepared fresh each day, as it takes only a few minutes to prepare it, and its activity is much greater when fresh. To do this, extract 5 grams of Jack-bean meal (60 to 100 mesh) with 100 c. c. of water for 5 to 10 minutes with frequent stirring, add 5 c. c. of N/10 HCl, and filter off the insoluble residue. The filtrate should react neutral to methyl-red. Ten c. c. of this solution is sufficient to convert 0.1 gram of urea to ammonium carbonate in less than one hour at ordinary temperature.

The above method has been in use at the laboratory for many months and has given entirely satisfactory results. Urease is specific for urea. It does not attack cyanamide itself, but cyanamide is readily hydrolyzed to urea in either alkaline or acid medium, and for that reason it is necessary to reduce the time of analysis to the minimum, avoiding strong acid or alkaline solutions or elevated temperatures as much as possible, in that way eliminating the only error that is likely to enter into the analysis.

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[5] E. K. Marshall, Jour. Biol. Chem. 14:283 (1913).

6. Agricultural Experiments.

A considerable number of agricultural experiments have been carried out by the laboratory in order to determine the availability as fertilizers of the various products which could be made at Muscle Shoals.

a. Pot tests.—In cooperation with the Bureau of Plant Industry, pot tests have been carried out, using beans and wheat grown in Norfolk Sandy Loam and Chester Loam, with the addition of various nitrogenous materials as fertilizers.

The results of pot tests can only be regarded as indicating in a very general way the agricultural characteristics of fertilizer materials. The tests in question showed that urea, ammonium nitrate, ammoniated superphosphate, and cyanamide are all reasonably satisfactory sources of nitrogen.

In agreement with the results of other investigators, dicyanodiamide was found to be very toxic to plant life. Guanylurea sulphate was also found to be toxic in heavy applications, although not so seriously as dicyanodiamide.

b. Field experiments.—In order to assist in making wise plans for the future utilization of the Muscle Shoals plant, fairly extensive field experiments with various nitrogenous materials have been carried out and are now in their third year. The crops selected for test have been cotton and corn, these being the most important crops in the whole of the agricultural region surrounding the plant. About 20 acres are under cultivation, divided into one-fortieth and one-twentieth acre plots with three different soil types. The complete and elaborate data obtained in these tests can not be presented in a limited space. A summary of the conclusions obtained up to date is given below.

The two nitrogenous materials which were used as standards in these tests were sodium nitrate and ammonium sulphate, and they proved to be of about equal value for both cotton and corn.

Ammonium nitrate was as readily available as sodium nitrate and gave similar responses to growth except that it was slightly more toxic to corn on one plot at the highest rate of application. The yields of both corn and cotton were so nearly the same with both fertilizers as to be within experimental error. It may be stated, then, that the two materials were essentially of equal value under the conditions used.

Cyanamide showed somewhat variable results, thus emphasizing the important rôle that soil and climatic conditions play in making its nitrogen available for plant use. When used on corn it was of practically equal value to the other forms of nitrogen. On cotton the yields were almost as good as with sodium nitrate and ammonium sulphate on one plot, inconclusive on a second, and very poor on the third and fourth. The primary explanation for the differences in responses with corn and cotton is attributed to the fact that corn can thrive on ammonium nitrogen, while cotton requires nitrates for its best growth.

It was found that cyanamide could be mixed with calcined phosphate, basic slag, or raw rock phosphate, but if used with acid phosphate must be applied separately.

Mixed salt, made from potassium chloride and ammonium nitrate, gave only fair results, but since the material was used on only one series of plots, and these were located on a rather unfavorable soil, it is felt that further experimentation is necessary to prove its true value. So far as observations during early growth were concerned, the mixed salt seemed to be as available and as satisfactory a source of nitrogen as sodium nitrate, but the yields failed to equal expectations.

Urea was one of the best materials used and seemed to be as readily available as sodium nitrate and equally as good in all respects as any other material used. Since urea is an excellent material physically and leaves neither a basic nor acid residue in the soil, it should prove to be an almost ideal nitrogen carrier for all types of soils except possibly the relatively few which have a feeble nitrifying power. Even under such conditions many plants would not be affected, for a few crops are thought to absorb urea directly and many utilize ammonia, which is rapidly produced from it in the soil. Except under conditions which are decidedly abnormal, urea nitrifies very rapidly, and unlike ammonium sulphate it does not contain an acid radical which is in itself detrimental to nitrate production.

In connection with the possibility that ammonium chloride may sometime become an important by-product of combined Solvay process and Haber plants, the behavior of this material as a fertilizer is of considerable interest. The results already obtained are by no means conclusive. At low concentrations the chloride ion sometimes seemed to show a stimulating effect to plant growth, and at high concentrations a slightly toxic effect. On the whole, however, the material does not seem to have properties very different from other good nitrogen fertilizers.

Double salt, made from ammonium nitrate and ammonium sulphate, showed results comparable with ammonium sulphate. It produced good responses to early growth of both corn and cotton, and the yields were so near those obtained with ammonium sulphate as to be within experimental error. The objection to this salt as a fertilizer material is that it is rather hygroscopic; in fact, the particular sample used in these experiments was almost as deliquescent as ammonium nitrate. Samples of this salt have since been prepared which were less hygroscopic, but even under the best conditions of manufacture the material is not entirely satisfactory in this respect.

Ammoniated superphosphate and ammonium phosphate are comparable with the equivalent mixtures of ammonium sulphate and acid phosphate. At one plot ammoniated superphosphate was somewhat slower to show results, but the later growth and yields were as good as with the other materials.

The direct comparisons between acid phosphate and calcined phosphate showed only slight differences in yields between the two materials. The rate of growth indicated that the former is slightly more readily available than the latter.

It will be seen from the above that cyanamide is a unique fertilizer material and frequently behaves in an entirely different manner from any other form of nitrogen used. When the conditions are just right it seems to be as valuable a source of plant food as any of the other forms of nitrogen, while under less favorable conditions it may be valueless or even injurious when used in large applications on crops that can not use ammonia as the main source of nitrogen. This emphasizes the importance attached to the transformations that must take place in the soil in order to make the material available for plant use. Almost immediately upon coming in contact with moist soil it apparently changes into calcium acid cyanamide, then free cyanamide, urea, and eventually into ammonia. A varying quantity of dicyanodiamide is produced as a side reaction. Of these transformation products, free cyanamide and dicyanodiamide are known to be toxic to certain soil bacteria, especially the nitrifiers, if present in quantities which may very well accumulate following fairly large applications of cyanamide. Nitrification can not, therefore, take place until these injurious compounds are so dissipated or changed as to no longer be present in sufficient concentrations to be injurious. Until this does occur the ammonia accumulates and the normal oxidation to nitrates is inhibited and the plant is forced to absorb ammonia or undergo nitrogen starvation.

The explanation of why the retarding period, following the use of cyanamide, lasts for a few days in one case and throughout the summer in another probably depends upon the particular compound primarily responsible for the retardation. If it is merely ammonia or free cyanamide, these materials will be quickly changed or dispersed and nitrate production may proceed normally. If it is dicyanodiamide, the effect may be expected to continue for a considerable period, since this compound is not only relatively insoluble but, more important still, it is not readily attacked to any extent by either bacteria or fungi. If the crop grown requires nitrate nitrogen, the growth will probably roughly parallel the amount of nitrate nitrogen present. If ammonia may be used, as in the case of corn, the growth may be more or less independent of the nitrification, provided the dicyanodiamide formation is not too great. This compound is probably not especially toxic, however, but merely not available for plants. A practical method of using cyanamide would seem to be to supply a nitrate form of nitrogen along with it, as has been done by others with excellent results. Even in this case it is important to make conditions such that as little as possible of the cyanamide nitrogen be converted into dicyanodiamide, since our present knowledge indicates that the latter material is not used as a plant food.

The importance of the rate and method of application of nitrogenous fertilizers has also been brought out by the experiments with corn. In many cases application of 10, and in some cases 20, pounds of ammonia per acre merely increased the growth of stalks without a corresponding increase in grain. To avoid this condition it has been suggested that the fertilizer be broadcasted or, at least, applied otherwise than in the row. The use of larger applications than 10 or 20 pounds of ammonia will also give satisfactory yields even if applied in the drill. If the smaller rates are used, the production of relatively large amounts of stover may be avoided by planting the corn thinner. Results obtained with standard fertilizers like sodium nitrate were identical in this respect with those obtained with the newer sources of nitrogen.

The results of the work up to date show, then, that ammonium nitrate, urea, double salt, ammoniated superphosphate, and ammonium phosphate are all readily available sources of nitrogen and practically equal in value to nitrogen in the form of sodium nitrate and ammonium sulphate. Mixed salt is probably as good, but the limited experimental work with this material still leaves a question as to its value. Ammonium chloride may exert a slight stimulating effect at the lower rates of application, and a slight toxic effect at higher rates of application, but on the whole seems to be about the same as ammonium sulphate except for special crops such as potatoes and tobacco. Cyanamide is not as satisfactory a nitrogen carrier as the common materials now in use, but where dicyanodiamide is not formed in sufficient quantities to inhibit nitrification the results are quite satisfactory. It should, however, be used in mixture with a nitrate form of nitrogen when applied to crops that are unable to grow well on ammonia nitrogen alone.

c. Bacteriological experiments.—One of the decomposition products of cyanamide in the soil is dicyanodiamide. This material is known to affect the growth of plants adversely, as already stated in connection with the pot tests described above. The exact mechanism of the toxic effect is still, however, a matter for further investigation, since it is possible that the adverse effect is due more to the destruction of useful bacteria in the soil than to a direct toxic effect on the plant itself.

As a matter of fact, experiments in the laboratory have shown, in confirmation of the work of others, that small concentrations of dicyanodiamide kill or inhibit the action of nitrifying bacteria. Using a garden soil rich in nitrifying bacteria it was found that one-tenth mg. of dicyanodiamide per 100 grams of dry soil slightly decreases the rate of nitrification of ammonium sulphate added to the soil, one-half mg. of dicyanodiamide decreases the rate very appreciably, and 2 mg. of dicyanodiamide completely prevents nitrification for more than 16 weeks.

The investigation is not completed, but these preliminary results are of interest. The conclusion can certainly be drawn that the agricultural undesirability of dicyanodiamide is partly due to its inhibiting effect on nitrification. Further work will be necessary to determine with precision the extent, if any, of a direct toxic action of dicyanodiamide on plant life.

The explanation of the fertilizer behavior of cyanamide given in the previous section was based on the assumption that the indirect toxic action of dicyanodiamide is what determines the very unique behavior of cyanamide as a fertilizer.

7. Miscellaneous Investigations.

One of the important by-products of a technical research laboratory lies in the solution of various miscellaneous side problems which may arise in the course of other investigations or which may particularly appeal to members of the staff of the laboratory as of sufficient general scientific value to warrant investigation without reference to their industrial application. The field of research into the unknown is full of adventurous possibilities, and the results of this incidental work may sometimes be of even greater social value than results obtained in the direct pursuance of the technical problems to which the main work of the laboratory is devoted.

a. Preparation and molecular weight of pure ozone.—In connection with the arc process the laboratory has studied the formation of ozone in the corona discharge as a typical gaseous reaction taking place in the path of an electric discharge. This work is described in a previous section, and has led quite naturally to the consideration of the chemistry of ozone in general.

One of the most interesting problems in connection with the chemistry of this material is its molecular weight. Measurements of the molecular weight of dilute ozone have always led to the molecular formula O_3. Results have been reported with concentrated ozone, however, which were taken as indicating the presence of O_4, or higher polymers. This problem has been attacked by the laboratory and the conclusion reached that the higher values reported can all of them be explained by the inaccuracy in the methods of analysis employed. The general method of analyzing for ozone consists in passing the gas containing it into potassium iodide solution where iodine is assumed to be liberated in accordance with the reaction

$$O_3+2KI+H_2O=O_2+2KOH+I_2.$$

The iodine is then titrated with thiosulphate.

The work of the laboratory in confirmation of the work of others has shown that, although this method of analysis gives correct results with low concentrations of ozone, with high concentrations of ozone it leads to results which are too high. This is explained by the fact that high local concentrations of alkali are produced with concentrated ozone, and in alkaline solution the reaction takes place so as to liberate more iodine than shown. The laboratory has come to the conclusion that all reports of molecular weight determinations giving higher values than O_3 can be explained by such an incorrectness in method of analysis.

In order to get a *direct* determination of the molecular weight of concentrated ozone, the laboratory has actually prepared 100 per cent pure ozone by successive fractional distillations, using liquid air as a refrigerant, and then determined the volume, pressure, temperature, and weight of this material in the gaseous form. The results have led to the formula O_3 for this material. The technique developed for this work has been complicated and full of interest, because of the appreciable rate of decomposition of ozone, and because of its very explosive nature, which has led to the abrupt termination of many of the experiments. It is hoped that a description of the work will be published in the near future.

This work has very definitely established the fact that concentrated ozone of formula O_3 can be prepared and the fact that previous claims of the existence of O_4 are not proved.

b. Pressure indicator for corrosive gases.—In order to measure the pressure of corrosive gases, such as nitrogen pentoxide and ozone, which can not be allowed to come in contact with metals or organic substances, or, in fact, almost any common materials except glass and quartz, the laboratory has developed an ingenious device. This consists of a glass tube closed by an extremely thin glass diaphragm. Arrangements are made so that the gas whose pressure is to be measured presses against one side of this diaphragm and air under adjustable pressure presses against the other side. A platinum spring is arranged so as to press against this diaphragm and moves up and down with it, and this platinum spring makes and breaks the connection in an electric circuit provided with an indicating instrument and a very small electromotive force. In this way it is possible to adjust the pressure of the air so as to counterbalance the pressure of the corrosive gas and then measure the air pressure with an ordinary manometer. It has been found possible in this way to measure pressures to a fraction of a millimeter of mercury.

A description of an earlier form of this apparatus which used a platinized diaphragm will be found in the Journal of the American Chemical Society 42: 1131 (1920). It is hoped that a more detailed description of the construction and behavior of the final form of apparatus will be published in the near future.

c. *Heat of adsorption of vapors on charcoal.*—An article on the heat of adsorption of vapors on charcoal suitable for gas masks has been published as a combined contribution from the laboratory and the Chemical Warfare Service (Jour. Amer. Chem. Soc. 42: 1146 (1920). Since the conclusions obtained have a bearing on the absorption of vapors by a catalytic material such as is used in the synthesis of ammonia, a summary of the conclusions obtained is presented below.

1. Measurements of the heat of adsorption of the vapors of some 11 organic liquids upon charcoal at 0° have been made over a considerable range. The resulting values have been shown to be reproducible and independent of the rate of adsorption of the vapor and of the previous history of the charcoal.

2. The heat of adsorption of all of these vapors can be represented very precisely as functions of the amount adsorbed by the expression $h=mx^n$, where h represents the heat of adsorption per normal c.c. of vapor, x the number of c.c. of vapor adsorbed, and m and n constants characteristic of each vapor.

3. The constant n in the above equation has been found to be nearly unity. The heat of adsorption, therefore, decreases but slightly with increasing amount of adsorption. In other words, there is but slight evidence of "fatigue" in the adsorptive forces.

4. It has been shown that this decrease (represented by $1-n$) is antibat to the boiling points of the liquids; that is, the liquids with relatively high boiling points exhibit a small value of $1-n$ and hence a slight fatigue. This is due to the fact that such liquids have high latent heats of vaporization.

5. m also varies relatively little from vapor to vapor. In general m and n tend to vary in opposite directions. In agreement with this the actual molal heats of adsorption of the various liquids measured

are not very different, varying between 12.0 cals. for ethyl chloride and 15.5 cals. for carbon tetrachloride.

6. The heats of adsorption of these vapors are very nearly the same on inactive as on active charcoal of the same kind.

7. Vapors containing halogens appear to react with the charcoal when warmed, so as to decrease the heat evolved by any subsequent adsorption of gas, without, however, affecting greatly the fatigue effect.

8. The net heats of adsorption; that is, the heats evolved above those corresponding to the latent heats of vaporization, are approximately of the same magnitude as the latent heats of vaporization.

9. The net heats of adsorption of c. c. of liquid are very nearly identical for all the liquids studied.

10. The net heats of adsorption are closely proportional to the heats of compression under high pressure. This indicates that the liquids are all attracted by the charcoal with substantially the same force, and that the net heat of adsorption is merely a heat of compression. The absolute value of this attractive force appears to be about 37,000 atmospheres where 1 c. c. of liquid is adsorbed on 10 g. of charcoal.

11. The molar adsorbability—that is, the number of c. c. of gas adsorbed at a fixed gaseous pressure (20 mm.)—is inversely proportional to the molecular volume of the liquid.

12. The molar adsorbability is inversely proportional to the net molar heat of adsorption. This, at first sight, surprising behavior is shown to follow necessarily from the previously mentioned regularities.

13. It is shown that all the above evidence indicates that the liquid films we have studied are all at least one and usually very many molecules thick, and this is confirmed by a consideration of the actual volume occupied by the liquid and the approximately known capillary volume and surface of the charcoal.

d. Theoretical studies.—Several theoretical studies in the field of mathematical physics have been published as contributions from the laboratory. These are: "Relativity Theories in Physics" (Gen. Elec. Rev. 23: 426 (1920); "The Entropy of Gases" (Jour. Amer. Chem. Soc. 42: 1185 (1920); "Statistical Mechanics Applied to Chemical Kinetics" (ibid. 42: 2506 (1920); "Note on the Theory of Monomolecular Reactions" (ibid. 43: 269 (1921); and "The Principle of Similitude and the Entropy of Polyatomic Gases" (ibid. 43: 866 (1921.)

In the near future it is expected that an article on "The Entropy of Electron Gas" and "Note on the Thermal Ionization of Metallic Vapors" will also be published.

e. Corrosion studies.—In connection with the design of apparatus for installation at Muscle Shoals to convert that plant into one suitable for fertilizer manufacture, a number of corrosion experiments have been made. The results obtained may be briefly summarized as follows:

(*a*) In sulphuric acid solutions 60° B. at 95° C. *duriron* is not corroded and *Monel* metal is very rapidly corroded.

(*b*) In a saturated solution of ammonium sulphate at 95° C. with an addition of 10 per cent of 60° B. acid, *duriron* soon forms a protective coating and *Monel* metal is fairly rapidly corroded. The solution in question is similar to what would be found in ammonium sulphate saturators.

(*c*) In strong ammonia solution at 95° C. both *duriron* and *Monel* metal are practically unattacked.

(*d*) In a saturated solution of ammonium sulphate at 95° C. or a saturated solution of ammonium sulphate to which ammonia has been added, *Monel* metal is practically unattacked, while *duriron* is rapidly attacked. This surprising fact agrees with the known use of ammonium sulphate for etching *duriron.*

(*e*) In concentrated phosphoric acid at ordinary temperatures *steel* and *aluminum* are rapidly corroded, *lead* and *Monel* metal slowly enough corroded so that they might be used as containers for this material, and *duriron* is uncorroded. *Monel* metal is somewhat more slowly corroded in concentrated phosphoric acid than *lead.* The rate of corrosion for *Monel* metal increases when the acid is diluted.

(*f*) At the temperature and concentrations which would be obtained in a saturator for making ammonium phosphate from concentrated phosphoric acid *duriron*, *Monel* metal, and *lead* are all somewhat corroded, but apparently not rapidly enough to prevent their use in such a connection.

C. POSSIBILITIES FOR FUTURE RESEARCH.

In the preceding section we have discussed the accomplishments in the field of research which the Fixed Nitrogen Research Laboratory has already completed or initiated. There are, however, almost limitless possibilities in the fields of nitrogen fixation and of the utilization of nitrogen compounds, and no future bounds to the extent and value of nitrogen research can be set. Improvements in existing methods of nitrogen fixation, investigations of proposed methods which have not yet come to commercial development, and perhaps, above all, further experimentation with different nitrogen-containing substances in order to make them more useful in agriculture and the arts should certainly continue for many years and probably for all time.

At the present moment, perhaps the greatest necessity for fixed nitrogen research lies in the investigation of methods for further decreasing the cost of fixation. The possibilities of doing this are very attractive, since the existing methods of fixation are relatively new, and there are a number of proposed methods which have not yet been given a thorough investigation.

A further important line of research is connected with the transformation of nitrogen-containing substances from one form to another. In particular, an important ideal to maintain in such research is that of ultimately putting atmospheric nitrogen directly into a form which can be assimilated by the animal body. In other words, we must look forward to the time when we can put atmospheric nitrogen in such a form that it can go at once into mixed feed for hogs and cattle. When we learn to do this at a reasonable cost, we could perhaps eliminate to a certain degree, at least, the expensive process of first putting the nitrogen into the soil and then taking it out again in the form of corn or other food material for live stock.

In the following paragraphs we can only briefly hint at some of the future possibilities in the field of nitrogen research.

1. The Haber Process.

The Haber process is the newest of all the methods of nitrogen fixation which are in actual commercial operation, and hence presents the greatest possibilities for future research and for the lowering of costs.

An analysis of the Haber process, as carried out in the Haber-Bosch form where the hydrogen is produced from water gas, shows that roughly 20 per cent of the total cost of manufacturing ammonia goes into the manufacture of the hydrogen used, and a further 50 per cent goes into the purification of this hydrogen, in order to make it suitable for passage through the catalyst. Since, then, 70 per cent of the total cost of the process goes into the manufacture and purification of hydrogen, it is obvious that this is the most vulnerable point of attack.

a. Cost of water-gas hydrogen.—Drastic lowerings of the cost of the manufacture of impure hydrogen by the water-gas process are not to be expected, because the method follows quite closely the well-known technique of water-gas manufacture. Improvements in the Bosch method of preparing hydrogen must come in the purification processes, and this is undoubtedly a field where further research will be profitable. Work to obtain the best catalyst for converting steam and carbon monoxide into hydrogen and carbon dioxide may well be continued, and the methods for removing small amounts of carbon monoxide, which remain after the conversion with steam, also furnish important possibilities for improvement. The laboratory is working in both of these fields, and it appears that such work can profitably continue for a number of years. As to the removal of carbon dioxide from the crude gases, it is felt that no great changes from the method of water scrubbing followed by alkaline scrubbing can profitably be introduced.

b. The use of electrolytic hydrogen.—The possibilities of the use of hydrogen produced by electrolysis are worthy of consideration. These are of particular importance owing to the simplicity of this method of manufacture and the purity of the product obtained.

In connection with electrolytic hydrogen, we must distinguish between two lines of attack, one being the electrolytic production of hydrogen on a large scale, where cheap water power is available, and the other being the utilization of the relatively small quantities of by-product electrolytic hydrogen which are allowed to go to waste in connection with the electrolytic manufacture of oxygen, caustic alkali, and bleaching materials.

For the production of electrolytic hydrogen primarily for the synthesis of ammonia only very cheap power and very large installations with large individual oxygen-hydrogen cells can be considered. For an installation to produce 11,000 tons of ammonia per annum the Nitrate Division has calculated that with power at 5 mills per kilowatt hour the costs of production (including overhead charges) would be about equal for electrolytic and water-gas hydrogen to be used in the manufacture of ammonia. With power at a higher figure the water-gas process would be more economical, and with power at a lower figure the electrolytic hydrogen would be preferable. This result is of great interest, since it shows that the possibility of such installations is limited to regions of cheap water power, and preferably to regions so located that the water power can not be sold at a higher figure for other industrial undertakings. It would seem that the Scandinavian power developments would be possible for such a utilization, as well as the proposed Muscle Shoals development and future power developments which may be made in America at a considerable distance from centers of industry which can absorb the power at higher figures. It should be pointed out that daily off-peak power could be used provided extra gas-holder capacity were installed, and that secondary power, available for a large fraction of the year, could also be used in the Haber process by shutting down during the dry months.

In connection with the figure just given for the comparative merits of the two methods of producing hydrogen, a number of important facts must be considered. The calculations in question were made on the basis of 10,000 ampere cells for the electrolytic production of hydrogen and oxygen. These cells are very much larger than any now on the market, and their size would decrease in the ratio of something like 1:3 the cost of installation, and hence the overhead charges. An experimental cell of this capacity, constructed by the Electrolabs Co., was tested by the Nitrate Division in cooperation with the Fixed Nitrogen Research Laboratory. Its performance was entirely satisfactory, and it is felt that the development presents great possibilities for the future.

A further consideration which must be kept in mind in considering the possibility of electrolytic hydrogen is the fact that no allowance was made in the calculations mentioned above for the value of the by-product oxygen that would be obtained. For a synthetic ammonia plant of any size this amount of by-product oxygen would be so great that its utilization could not be fitted into the present market for oxygen. In this connection, it would be desirable to investigate the possibility of utilizing larger quantities of low-cost oxygen, presumably in connection with metallurgical processes. This field of research is one which has already been a matter of great interest to the Bureau of Mines of the Department of the Interior.

The possibilities of producing hydrogen and caustic alkali simultaneously on a large scale by electrolysis are also deserving of investigation.

c. The use of by-product hydrogen.—As to the existing sources of waste hydrogen, a consideration of the possibility of their utilization for ammonia manufacture is very important. Such waste hydrogen now occurs in connection with the electrolytic manufacture of bleaching materials, caustic alkali, and oxygen. The individual amounts to be considered vary over a range of 20,000 to 100,000 cubic feet per day at the different plants, but the total amount going to waste in America is large enough to be a factor of importance.

For the utilization of these relatively small quantities of waste hydrogen, methods of operation quite different from those in large water-gas installations must be considered, since the economies which can be introduced by large-scale installations are in this case not possible.

For small units, such as would have to be used in connection with these small quantities of waste hydrogen, simplicity of operation would be of prime importance. This can perhaps best be achieved by working along lines partially developed in France by M. Claude.

In the Claude variation of the Haber process, very high pressures, in the neighborhood of 1,000 atmospheres, are used. With such high pressures the percentage conversion to ammonia is greatly increased, and the size of the apparatus to produce a given total yield is greatly decreased, partly because of this increased percentage conversion, but largely because of the increased amount of gas which it is possible to put through an apparatus of given volume at high pressure. This in itself is a considerable simplification of the apparatus. It should be noted, moreover, that the engineering difficulties in constructing an apparatus to stand the very high pressures are much reduced by the small size of the equipment.

A further simplification can be introduced, because the high percentage of ammonia obtained makes it feasible to eliminate circulation through the catalyst system. Instead of this the high-pressure gas is passed directly through a catalyst chamber with the production of a large percentage of ammonia, which is then removed as liquid ammonia, the remaining gas is then passed through a second catalyst chamber of smaller capacity, and the ammonia synthesized again removed. After the passage of the gas through two or three such successive steps, it is considered economical to reject the unsynthesized gas which will contain all the impurities, such as argon, which have been introduced with the nitrogen.

The high percentage of ammonia obtained and the high pressure introduce a further simplification of the methods of ammonia removal, since a large fraction of the ammonia can be liquefied under these conditions at temperatures which can be obtained with ordinary cooling water.

Another point of importance in connection with the use of waste hydrogen is that, since the hydrogen would otherwise be thrown away, it is allowable, at least as a temporary expedient, to produce the mixture of nitrogen and hydrogen simply by the burning of enough hydrogen with air to give the desired mixture of 3 parts of hydrogen to 1 of nitrogen. This can be carried out with relatively simple burners, and the bulk of the water formed removed by condensation, followed by chemical treatment for the remainder.

It will thus be seen that in the case of waste hydrogen utilized at high pressures the apparatus becomes very simple, consisting, first, of a burner to produce the mixture of hydrogen and nitrogen, followed by a water-removal system, a compressor to 1,000 atmospheres, and a series of two or three catalyst containers each followed by a water-cooled condensing coil for removing liquid ammonia.

One of the main difficulties of the process proposed by Claude is the construction of the compressor for delivering gas at 1,000 atmospheres. The chief trouble seems to arise at the high-pressure stuffing box, which has to be frequently repacked. Experiments have been planned at the laboratory for overcoming the difficulties in the compression of gases to very high pressures.

d. Production of hydrogen from methane.—Another possibility for the production of cheap hydrogen would be the utilization of the methane in natural gas. This has been proposed by a number of persons, and some patents have been already taken in this field.

At high temperatures methane dissociates into carbon and hydrogen in accordance with the reaction

$$CH_4=C+2H_2-21{,}700 \text{ cal.}$$

Since this dissociation is endothermic, it increases with rising temperature, and at 1,000° C. and 1 atmosphere pressure the dissociation is already in the neighborhood of 99 per cent complete. If it were possible to obtain at the same time hydrogen and a deposition of carbon in a form suitable to replace the lampblack now produced for use in rubber manufacture by the wasteful burning of natural gas, the advance would be a very important one both for industry and for the conservation of natural resources.

e. Ammonia catalyst.—Of course, the heart of the Haber process will always be the catalyst for the synthesis of ammonia from nitrogen and hydrogen. Further research along this line can profitably continue for many years. In particular, the possibility always presents itself of producing a catalyst which will operate at a low enough temperature to give almost complete union of nitrogen and hydrogen to form ammonia. The main obstacle in the way of obtaining such low-temperature catalysts seems to be the probability that they will be easily poisoned, since it is a general experience with all contact catalysts that poisoning effects become more serious as the temperature is lowered. Nevertheless, the possibility of a catalyst which would work in the neighborhood of room temperature and at low pressures to produce large yields of ammonia must always be kept in mind.

Another important phase of catalyst research lies in a determination of the actual mechanism of the catalytic action. This is an extremely baffling problem, apparently more so for ammonia catalysis than for many other contact processes. On the ultimate solution of this highly scientific problem, however, we must depend for a secure mastery of the technical synthesis of ammonia.

2. The Cyanamide Process.

The cyanamide process is an older development than the Haber process and one in which there is less possibility of variation in the method of carrying out the different steps. For this reason there seems to be less possibility of reduction in costs than in the case of the Haber process.

a. The cost of carbide.—The main source of expense in fixing nitrogen by the cyanamide method is the cost of the carbide. With power at 4 mills per kilowatt hour, the cost of power for the carbide manufacture is one-third the total cost of manufacturing cyanamide, while the cost of limestone, coke, coal, and electrodes is approximately a quarter of the total figure. It is evident that the most important point of attack for the application of research to the cyanamide process is to see if the carbide can be more efficiently utilized or more cheaply manufactured.

As to the efficiency with which the carbide is utilized, it is now possible with good practice in the nitrifying ovens to utilize 85 per cent of the total carbide present. This presents the possibility of some improvement, but still not a drastic one. Nevertheless, further research into the methods of nitrifying will be a desirable line of work in the future.

As to the cost of carbide manufacture, it is evident, since the cost of the raw materials is pretty well fixed, that the main improvement would have to come through a decrease in power consumption.

Our present thermodynamic knowledge concerning the reaction

$$CaO+3C=CaC_2+CO-105,000 \text{ cal.}$$

is so limited as to make an exact determination of the possibilities of power saving impossible. The heat absorbed by the reaction at room temperature, as indicated above, is believed to be in the neighborhood of 105,000 calories per mol of carbide formed, but this figure is by no means certain. Furthermore, although some attempts have been made to measure the equilibrium pressure for the above reaction, the results were not very concordant and were obtained at temperatures considerably below the fusion point of carbide, and, hence, considerably below the temperature of actual furnace operation. Hence, almost nothing is known as to the value of the important thermodynamic quantity, namely, the free energy of the reaction.

This lack of knowledge prevents any exact estimate of the economies in carbide manufacture which might theoretically be achieved. Further research into the mechanism and thermodynamics of the carbide reaction should certainly be carried out. The work should include a study of the possible formation of a subcarbide as well as a determination of the heat and free energy of the reaction.

Although, as just pointed out, lack of data makes it impossible to make an exact estimate of the efficiency of carbide manufacture, nevertheless a rough comparison of the actual and theoretical thermal inputs is possible. The heat of reaction at 25° C. can be taken as 105,000 calories. Taking the most probable values for the specific heats of the substances involved, the heat of reaction at the assumed reaction temperature of 2,000° C. comes out 105,400 calories. To this figure we must add 64,200 calories as the heat necessary to raise the temperature of the carbon and lime from 25° C. to the reaction temperature 2,000° C. and obtain as the total heat input necessary for carrying out reaction 169,600 calories. At the Muscle Shoals plant in the test run on the carbide furnaces the actual electrical input per mol of carbide formed was found to be 220,000 calories. This would indicate that the efficiency of the electric furnaces was as high as is usual in electric-furnace practice. As already pointed out, however, more exact knowledge both of the heat of reaction and of the free energy of the reaction will be necessary before this conclusion can be definitely accepted.

A further consideration that must be kept in mind in connection with the possibility of improving the method of carbide manufacture is the fact that the carbon monoxide which now escapes from the open furnaces is not utilized. Assuming that this carbide escapes at a temperature of 1,000°, it would be possible to save about 8,000 calories by utilizing the sensible heat of this gas. It would further be possible to obtain 68,400 calories per mol by burning the carbon monoxide to carbon dioxide. It will thus be seen that the total heat wasted by lack of utilization of the carbon monoxide is in the neighborhood of one-third of the electric energy put into the furnace.

As to the methods of utilizing the sensible heat and the heat of combustion of the carbon monoxide, the first thought would be to use some form of shaft furnace in which the incoming charge would be heated by the escaping gas, air being led in at intervals to burn the carbon monoxide. Although experiments have been tried along these lines, the results are not known. It is evident, in the first place, that such shaft furnaces would be much more complicated than the present simple open furnaces, and, in the second place, it must be pointed out that experimentation along these lines is a very expensive matter. since it has but little value unless carried out on a very large scale.

Attention may also be called to the possibility of utilizing the carbon monoxide as a fuel either for steam generation or for burning limestone or other uses about the plant. This would, of course, necessitate some form of closed furnace which would prevent the carbon monoxide from coming in contact with the air. This would greatly increase the difficulty of furnace operation. It should be pointed out that the heat of combustion of the carbon monoxide produced in the carbide furnaces is about five times as much as would be needed for burning the lime used.

The above remarks indicate that there are some possibilities of cheapening the cost of carbide manufacture.

b. Use of other carbides and cyanamides.—Another method of trying to modify the cyanamide process would be to consider the possibilities of other materials analogous to calcium cyanamide. In this connection the suggestions of Dr. S. Peacock (U. S. patent 1,134,412, April, 1915) for using magnesium cyanamide are of interest. The advantage that Doctor Peacock claims for such a possibility is the considerably reduced temperature at which the process could be carried out. On the other hand, it must be noted that owing to the high cost of the magnesium it would have to be utilized over and over again.

In connection with the possibility of utilizing other materials than calcium, it is hoped that the work at the laboratory on various reactions to form cyanides and cyanamides of calcium, sodium, magnesium, and other elements may ultimately suggest important possibilities.

c. Disposal of autoclave sludge.—Another important thing for investigation in connection with the cyanamide process is the matter of utilizing the autoclave sludge. The enormous amounts of this material that are formed is a serious problem. Some possibilities for its utilization have already been suggested, but it may be that further thought along this line will open up new fields for research.

3. The Arc Process.

The arc process is the oldest and in many ways the simplest method of nitrogen fixation. Its main handicap is the large amount of power necessary for fixing a ton of nitrogen, the power required by this method being some 67,000 kilowatt hours per ton of nitrogen, as compared with about 15,000 kilowatt hours per ton of nitrogen fixed by the cyanamide process, 4,500 kilowatt hours per ton of nitrogen fixed by the Haber-Bosch process, and 18,000 kilowatt hours per ton of nitrogen fixed by the Haber electrolytic process. It is evident that a reduction in power consumption would be the most important improvement that could be made in the arc process.

a. Power consumed in the arc process.—The essential reaction in the arc process is

$$\tfrac{1}{2}N_2+\tfrac{1}{2}O_2=NO-21{,}600 \text{ cal.}$$

where the heat of reaction at 25° C. is in the neighborhood of 21,600 calories. The actual energy input used in producing 1 mol of nitric oxide in existing arc installations is in the neighborhood of 865,000 calories. This great discrepancy between these two figures has often led to the belief that the arc process was actually operating very inefficiently and that there were enormous possibilities for improvement which might be achieved by some more fortunate design for the furnace. Further consideration, however, shows that such a belief neglects important aspects of the problem.

The arc process in any of its present forms must be regarded essentially as a thermal process. The function of the electric discharge is primarily to produce a temperature high enough so that the equilibrium corresponding to the equation written above will be shifted to an appreciable extent in the direction of forming nitric oxide. Even if the discharge should have the effect of furnishing some special electrical conditions which favor the formation of nitric oxide, nevertheless the percentage of nitric oxide which escapes from the high temperature zone will undoubtedly be determined by the temperature gradient where the hot gases are mixed with colder gases to " freeze " the yield. Under the circumstances we can obtain the clearest picture of existing arc processes if we think of them as methods by which air is raised to a high enough temperature so that an appreciable quantity of nitric oxide can be formed, followed by a quick cooling of the reaction mixture, in order to prevent the redissociation of the nitric oxide.

Under these circumstances, to calculate the thermal efficiency of existing arc processes, we must compare the actual energy input not with the heat of reaction at room temperature but with the amount of heat necessary to raise the air to the reaction temperature plus the heat necessary to make the reaction occur. It will be found that much the largest quantity of heat is used in heating the air to the reaction temperature and that the amount absorbed in the actual reaction is only a small fraction of the total. Computations made on this basis show that the thermal efficiency of existing arc processes is much higher than would at first be supposed, perhaps in the neighborhood of 50 per cent. Calculations indicating this fact will be found in the description of the arc process in Chapter IV. It may be safely concluded that radical increases in thermal efficiency will not be possible with the existing type of arc process.

Such minor improvements as the use of air enriched with oxygen in order to secure a more favorable equilibrium in the arc, the elimination of moisture, which has a deleterious effect on the yield, and improvements in electrical or mechanical design of the furnaces are worthy of consideration, but revolutionary improvements from work carried out along such lines can not be expected.

In connection with the calculations of thermal efficiency mentioned above, attention must be called to the fact that the computed values are only approximate. This is due to our lack of knowledge as to the actual temperatures in different zones of the arc, as to the fraction of the air actually heated to the different temperatures, and as to the rate of diffusion of the nitric oxide from the reaction zone to regions of low enough temperature to prevent redissociation. Further research into the actual properties of an arc discharge would be extremely informing and should be carried out.

b. Investigation of other types of discharge.—Although the existing arc processes must be considered substantially as thermal in nature, this does not mean that the investigation of the electrical effects of discharges should be neglected, and this has been the main field toward which the Fixed Nitrogen Research Laboratory has desired to turn its attention.

By working with low-temperature arcs or by investigating other types of electrical discharge, such as that in the corona, it may be possible to find conditions under which the electrical input can be made more nearly equal to the actual heat of reaction, 21,600 calories. It must be definitely pointed out, however, that such investigations, if successful, would lead to processes of an entirely different kind from those that will be obtained by any modifications in the mechanical or electrical features of existing arc furnaces. In this connection the high yields obtained by Haber and König (Zeit. f. Electroch. 1907, 13: 725; 1908, 14: 689) with low-temperature arcs must be regarded with interest. The yields were considerably higher than corresponds to the thermal equilibrium at the temperatures used. The whole question of the way chemical reactions take place in the path of an electric discharge will be a fruitful one for investigation for many years to come.

c. Absorption of products.—Next to the cost of power the largest expense in the arc process occurs in connection with the absorption of the very dilute nitrous gases in water. The high dilution of these gases necessitates very large absorption towers. Further research on the removal of dilute oxides of nitrogen should be undertaken.

In this connection, important work was carried out for the Nitrate Division during the war by Noyes and Burdick on the use of a catalyst for hastening the reaction between nitric oxide and oxygen to form nitrogen dioxide.

It might also be desirable to consider the possibilities of concentrating the nitrogen dioxide obtained from the arc process by preliminary adsorption with silica gel or other solid adsorbent.

4. The Cyanide Process.

The cyanide process is still in so undeveloped a stage that many possibilities for research are presented. As already pointed out, this research would be of two kinds—first, chemical research into the nature of the actual reactions which are taking place; and, second, engineering research into methods of handling the charge in a reasonably automatic manner and without such a rapid destruction of the retorts as is now the case.

Attention must also be paid to various modifications in the cyanide process, such as that proposed by Mehner, and the possibilities of other reactions to form cyanides, nitrides, cyanamides, or similar compounds. The possibility of recovering cyanides from blast furnaces should also be kept in mind. Important research on the cyanide process can undoubtedly continue for years.

5. Other Processes of Nitrogen Fixation.

In Chapter IV a number of other methods of nitrogen fixation have been considered and these all furnish fruitful fields for research.

It seems quite possible that entirely new methods of nitrogen fixation may become of actual commercial significance within the next couple of decades. Proposals along these lines should all be given fair consideration. In particular, more attention might well be paid to the aluminum nitride process.

6. The Properties and Methods of Transforming Nitrogen Products.

Research on the best methods of transforming nitrogen-containing substances from one form to another, and on the properties of different nitrogenous compounds, can probably be continued almost indefinitely. The work in this field may be considered under two different headings: (*a*) Nitrogen in inorganic compounds, and (*b*) Nitrogen in organic compounds.

a. Nitrogen in inorganic compounds.—In an earlier part of this chapter we have discussed at considerable length the researches carried out by the laboratory on different inorganic nitrogenous compounds. The work in this field is perhaps better rounded out than in any other field that the laboratory has investigated. Nevertheless, further progress can undoubtedly be made. The fundamental transformation steps, such as the autoclaving of cyanamide to produce ammonia and the oxidation of ammonia to produce nitric acid, will bear further research.

The problem of changing nitrate nitrogen back into ammonia nitrogen is one which will probably never have any commercial significance, since, with the decreasing supply of Chilean saltpeter, ammonia nitrogen is probably always going to be cheaper than nitrate nitrogen.

A search for further nitrogenous compounds suitable for use in agriculture is one which must not be neglected. In general, it is believed, in agreement with the view so long advocated by Doctor Whitney, of the Bureau of Soils, that we should try to work in the direction of the most concentrated fertilizer materials. In this connection ammonium phosphate is, of course, an extremely important substance, and improvements in methods of phosphoric acid manufacture are of fundamental importance for the nitrogen problem. The high concentration of ammonium nitrate as a fertilizer material must also not be forgotten, and further methods of making this material nondeliquescent should be investigated. Urea is a very hopeful substance for fertilizer use, and its manufacture should be undertaken and improved.

Research on the oxides of nitrogen is desirable. The present methods of handling nitric oxide are far from ideal. This substance is the product obtained both from the arc process and from the oxidation of ammonia. Up to date it has only been handled in a single way. It has been led, together with excess air, through water absorption towers, where it is absorbed to make dilute nitric acid in accordance with the reactions

$$NO+\frac{1}{2}O_2=NO_2 \quad (1)$$
$$3NO_2+H_2O=2HNO_3+NO \quad (2)$$

the nitric oxide formed by reaction (2) being again reoxidized in accordance with reaction (1). The slow step in this chain of reactions is the oxidation of nitric oxide to nitrogen dioxide, and this has led to the necessity of very large absorption towers in order to give time for this step to take place.

Attention has already been called to the desirability of investigating the proposal of Noyes and Burdick, that catalyst chambers be introduced in series with small water absorption towers in order to speed up the absorption process. Investigations of this possibility on a semicommercial scale would be of great interest. The possibility of concentrating nitrogen dioxide by preliminary adsorption on silica gel or other solid adsorbent has also been mentioned.

The direct utilization of nitrogen dioxide as an oxidizing agent, nitrating agent, or as a constituent of explosives should not be neglected. The possibilities of treating nitrogen dioxide with ozone to form nitrogen pentoxide should be further investigated, and more should be known about the properties of nitrogen pentoxide which might prove an important reagent for organic chemical syntheses.

b. Nitrogenous compounds containing nitrogen in the organic form.—There are a wealth of possibilities in connection with the organic chemistry of nitrogen. In this connection it is believed that cyanamide is one of the most important starting points for organic chemical preparations, and further research into the chemistry of cyanamide will be of great value.

As to the possibilities of utilizing cyanamide for organic syntheses, attention is called to the fact that the cyanamide linkage is fundamental in guanidine and its derivatives nitroguanidine, aminoguanidine, biguanide, etc., and in thiourea and its derivatives. It is also contained in the drugs, barbituric acid, veronal, and other derivatives, and purine bases such as guanine, theobromine, theophylline. It is furthermore fundamental in the guanidine type of aminoacids, such as glycocyamine, arginine, histidine, creatine, etc. This list of chemicals containing the cyanamide linkage indicates that this material may become an important starting point for organic syntheses. Of course, it must be pointed out that the cyanamide linkage may not be the most difficult part of the synthesis.

Further compounds for which cyanamide has been suggested as a starting point include thiocyanates, formic acid, and salts of color acids with compounds of the cyanamide type.

With regard to the organic chemistry of nitrogen, it may be pointed out that the synthesis of proteins may, from one point of view, be regarded as the main reason for the fixation of atmospheric nitrogen, since fixed nitrogen will largely be used for increasing the yields of corn and other foodstuffs. This immediately suggests the possibility of getting nitrogen into a form where it can be made part of the animal diet without the necessity of taking the agricultural step. In this connection various possibilities present themselves.

One possibility is that of feeding animals with nitrogen in a simpler form than that of proteins. Experiments have been carried out along such lines, but decisive conclusions have apparently not been reached. The general opinion is gained from the literature that it is not feasible to supply any appreciable fraction of the nitrogen in the animal diet in the form of ammonium sulphate or other ammonium salts. (See Emil Abderhalden Z. Physiol. Chem. 96; 1–147 (1915).) As to the possibility of using slightly more complicated compounds of nitrogen, such as urea, there seems to be more difference of opinion. Abderhalden claims that urea is worthless as a nitrogen foodstuff, while the later work of Voltz (Biochem. Z. 102; 151 (1920)) on the feeding of lambs indicates that 50 per cent of the nitrogen can be given in the form of urea. Voltz claims that the amides are to be reckoned as digestible forms of nitrogen.

Even if urea or some other cheap and simple form of nitrogen could be used as a part of the nitrogen diet, it could never entirely replace the proteins, or, rather, the amino acids, into which the proteins are broken down in the process of digestion, since it has been definitely shown that some amount of each of the six different types of amino acid must be present in a complete diet. This, of course, suggests the desirability of investigating methods of synthesizing some of the different types of amino acid by a method which would be commercially feasible and would lead to the production of material suitable as a partial constituent of mixed feeds.

A method of synthesizing proteins without resorting to large-scale agriculture would be to grow yeast in a culture containing ammonium sulphate and sugar. Experiments along this line have been reported, using sugar obtained from the hydrolysis of sawdust, together with ammonium sulphate, with the idea of ultimately feeding the yeast to cattle. Such a method of synthesizing proteins can not be considered as strictly nonagricultural, since the growing of the yeast plant may be considered as a "farming" operation, even if it does occur under laboratory control. Nevertheless, the suggestion is very interesting and the possibilities along these lines should certainly be investigated.

7. Agricultural Research.

Further agricultural research on the behavior of nitrogenous compounds in the soil is a matter of great interest. The determination of their nutritional value for different crops, their toxicity to plant germination and plant growth, their effect on the helpful bacterial population of the soil, and their transformation in the soil both by chemical and bacteriological action, should all be investigated. These problems, moreover, merge into a general consideration of the science of soil fertility, which is one of the most fundamental practical problems faced by the whole human race.

CHAPTER VII.

FIXED-NITROGEN ACTIVITIES OF UNITED STATES GOVERNMENT.

A. INTRODUCTION.

The importance from a military standpoint of providing facilities for the fixation of atmospheric nitrogen for use in the manufacture of explosives, which would make the United States, to some extent at least, independent of foreign sources of supply of this indispensable material, had long been recognized by military authorities and had been repeatedly urged by the representatives of the Ordnance Department.

In his report to the Secretary of War for the fiscal year ending June 30, 1915, the Chief of Ordnance, in adverting to the dependence of the United States upon a foreign country for the prime essential of all its explosives, namely, nitrate of soda, said in part:

> In a country of even the very large natural resources of the United States there are nevertheless some articles, essential in time of war, for which it is dependent upon foreign sources of supply. If these sources are so placed as to necessitate ocean transportation, the possibility of being cut off from them is great enough to call for provision against it. I do not know of any article of this class which at the present time should cause more concern with reference to the war-time supply than should nitric acid. The principal ingredient of the gunpowder of the present day, as well as of certain other explosives, is formed by treating ordinary cotton with nitric acid. The nitrogen in the nitric acid is obtained from sodium nitrate, which comes from Chile, and the country is therefore dependent for its powder manufacture upon Chile. Some attempt has been made to place in storage a sufficient quantity of sodium nitrate to serve the country during a considerable period of interruption of supply; but there is no difficulty in saying now that the amount in store would produce a quantity of powder which would be insignificant in comparison with the requirements of a war, although it would undoubtedly be serviceable in tiding the country over a period which might be sufficient for setting in operation other methods of securing nitrogen for nitric acid, which would have been prepared in advance.
>
> These facts point to the necessity for inquiry into the possibility of the establishment within the limits of the country of a source of supply of this war essential. Fortunately the possibility exists. There are in successful operation in Europe in several countries plants for the fixation of atmospheric nitrogen and rendering it available for use in the manufacture of nitric acid.

These plants require for their manufacturing processes electric current in large amount. In order that they may be commercially successful the current must be very cheaply obtained, and it is generally thus cheaply obtained by the employment of water power. In this country the expense of the employment of steam-generated electric current would not, in my opinion, be such as to render this method prohibitive for such an amount as would be required for the manufacture of nitric acid for gunpowder and other military explosives.

I believe that a steam plant could be established which would contribute effectively to the supply of the nitric acid which would be needed in the manufacture of powder for the current prosecution of a considerable war; but the expense, while not prohibitive, would still be such that this kind of a plant could probably not maintain itself commercially in ordinary times as against the production of nitric acid from imported nitrates, and the plant would, therefore in all probability remain in disuse in peace time, being held in reserve for time of war. Such a solution of the problem would be advisable if no better solution could be found, but the possibility of a better solution is apparent. There are in the United States various opportunities, under the control of the Federal Government, for the development of great water power. Some of these, I am informed, are such as to warrant their development for the purpose of power alone, and others would justify development for power in connection with or as an incident to the improvement of navigation. Estimates have been made of the cost of the power which would thus be made available, and have shown it to be such as to permit the fixation of atmospheric nitrogen in compounds which could be used in the manufacture of nitric acid at such prices as to enable water-power plants to maintain themselves in successful competition in the nitrate industry with foreign sources of supply of nitrates.

During the next year the several methods of nitrogen fixation were considerably studied under the direction of the Chief of Ordnance. Upon reading an article in the July 1, 1915, edition of Leslie's Illustrated Weekly on the subject of the manufacture of nitrates from atmospheric nitrogen, included in which was a picture of the American Cyanamid Co.'s Niagara Falls, Canada, plant, the Chief of Ordnance, on July 22, 1915, addressed a letter to the American Cyanamid Co., Canada, stating that "* * * this department would appreciate any information you may feel disposed to give which would aid it in reaching a conclusion as to the desirability of establishing a plant within the limits of the United States, and the feasibility of utilizing any of its existing water powers." Under date of July 30, 1915, the president of the American Cyanamid Co. replied confidentially advising of his company's plant, process, capacity, etc.; of the nitric acid situation in Germany at that time; and of the general conditions under which his company would aid the Government in an attempt to secure an independent supply of nitric acid. Following this the Chief of Ordnance and the president of the American Cyanamid Co. were quite continually in touch with each other either through correspondence or personal conference.

During this year, 1915–16, there were introduced into Congress several bills looking toward the establishment of nitrogen fixation processes; and the subject in general attracted much attention in debate and in the public press throughout the country. Although none of these bills became law, Congress was now agitated over the subject and numerous proposals of legislation were made, looking toward an appropriation of public moneys for the furtherance of fixation processes. The culmination of this was the incorporation into the national defense act, approved June 3, 1916:

> SECTION 124. Nitrate supply.—The President of the United States is hereby authorized and empowered to make, or cause to be made, such investigation as in his judgment is necessary to determine the best, cheapest, and most available means for the production of nitrates and other products for munitions of war and useful in the manufacture of fertilizers and other useful products of water power or any other power as in his judgment is the best and cheapest to use; * * *.
>
> The sum of $20,000,000 is hereby appropriated out of any moneys in the Treasury not otherwise appropriated, available until expended, to enable the President of the United States to carry out the purposes herein provided for.

The Secretary of War was then designated to carry out the provisions of this section (sec. 124, nitrate supply) of the national defense act.

At the request of the Secretary of War the president of the National Academy of Sciences, in cooperation with the American Chemical Society, appointed a committee of scientists and engineers to determine the best, cheapest, and most available means for the production of the desired nitrogenous materials. This committee, the personnel of which was Dr. Arthur A. Noyes, chairman; Dr. Leo H. Baekeland, Mr. Gano Dunn, Dr. Charles H. Herty, Dr. Warren K. Lewis, Mr. Michael I. Pupin, Dr. Theodore W. Richards, Dr. Elihu Thompson, Dr. Willis R. Whitney, submitted a preliminary report on June 2, 1916, a summary report on January 6, 1917, and its complete final report on January 20, 1917.

This report recommended briefly that (1) a sufficient supply of saltpeter (Chilean nitrate) should be imported and stored here as would constitute a safe provision for the first year of hostilities; (2) the Government should prepare to utilize in a war emergency the large domestic production of coke-oven ammonia by erecting a plant for purifying coke-oven ammonia and converting it into nitric acid; (3) the Government should provide for the development of processes for the fixation of atmospheric nitrogen on as large a scale as possible by developing at a suitable location as much hydroelectric power as is possible with the appropriation available, and sell this power at cost to private companies for use in fixing atmospheric nitrogen.

General opinion was probably in accord at the time with this recommendation regarding a large water-power development and many sites for plants were being urged for selection in view of their potential water power. The President, therefore, on January 15, 1917, appointed the so-called Interdepartmental Board, consisting of the Secretaries of War, Interior, and Agriculture, to consider sites for nitrate plants. In the early part of 1917 this board made a journey throughout the southern and eastern portions of the United States holding hearings en route and examining all of the more prominently mentioned sites. No formal report was made, however, as the continuance of this investigation came to an abrupt end due to the turn in events.

On April 7, 1916, the Secretary of Interior offered the Secretary of War the aid of the Interior Department in any capacity in which it would be useful for national preparedness. Accordingly, during April and May the chief chemist of the Bureau of Mines, of the Department of Interior, had several informal conferences with the Chief of Ordnance on the question of nitrate supply, and in August at the proposal of the Secretary of War that qualified representatives be sent abroad to study the methods of manufacture of nitric acid, otherwise than from sodium nitrate, followed in the various countries of Europe, the Secretary of Interior designated Dr. Charles L. Parsons, of the Bureau of Mines, and recommended Mr. Eysten Berg, an engineer who had had exceptional opportunity for observing and studying fixation processes, as these representatives. Both were accordingly appointed chemical engineers in the Ordnance Department for the last three months of 1916, during which time they visited plants in France, Italy, England, Norway, and Sweden.

The large mass of information obtained by these representatives formed the basis of study for the recommendations made by the National Academy Committee on January 20, 1917, mentioned above.

Mr. Berg's report of January 15, 1917, showed that the most prominent processes were the arc, cyanamide, and Haber, all of which were used to some extent in Europe. He further described the processes, with their respective power requirements.

The first formal report from Doctor Parsons was submitted on January 27, 1917, and a subsequent one on April 30, 1917. In these reports special emphasis was laid upon the rapid development in the United States of processes for the direct synthesis of ammonia from nitrogen and hydrogen, for its synthesis through the formation of cyanide as an intermediate product, and for the oxidation of ammonia to nitric acid. Attention was called to the process developed by the General Chemical Co. for the synthesis of ammonia by the direct combination of nitrogen and hydrogen at lower pressures than those previously deemed necessary and contemplated by the Haber patents. A tentative proposal from the General Chemical Co. of an agreement whereby that company would grant to the Government of the United States the use of its processes and designs for apparatus for the synthesis of ammonia and for the oxidation of ammonia to nitric acid upon very liberal terms was also included in the report.

All these processes of promise had been previously brought out, however, and on March 9, 1917, the Secretary of War appointed a new committee, called the "Nitrate Supply Committee," to secure an opinion based upon a comprehensive review of all the facts collected up to that time by the several agencies whose aid had been invoked. This committee consisted of the following: Brig. Gen. William Crozier, chairman, Rear Admiral Ralph Earl, Brig. Gen. William M. Black, Mr. F. W. Brown, Dr. Leo H. Baekeland, Mr. Gano Dunn, Dr. Chas. H. Herty, Dr. William F. Hillebrand, Dr. Arthur A. Noyes, Dr. Chas. L. Parsons, and Dr. Willis P. Whitney.

After giving careful consideration to all information available, and after duly weighing the several purposes of the national defense act, the committee recommended the following action:

I. That the Government negotiate with the General Chemical Co. for the right to use its synthetic ammonia processes.

II. That contingent upon satisfactory result of such negotiations, there be set aside from the $20,000,000 appropriated, such sum, estimated at about $3,000,000, as should be necessary to build a plant to produce by that process about 60,000 pounds of ammonia per 24-hour day; location, southwest Virginia preferably.

III. That out of the same appropriation, $600,000, or as much more as needed, be set aside for building a plant for producing by oxidation of ammonia about the equivalent of 24,000 pounds of 100 per cent nitric acid per 24-hour day.

IV. That the War Department proceed at the earliest practical date with the construction of the oxidation plant and, contingent upon satisfactory arrangements with the General Chemical Co., with the construction of the synthetic ammonia plant also.

V. That the Government negotiate with the Nitrogen Products Co. with the view to a contract for the right to use that company's patents and proceed with experimentation looking toward the industrial development of the Bucher process for production of ammonia through cyanide; and that contingent upon satisfactory arrangement as above a sum not over $200,000 be allotted out of the nitrate supply appropriation.

VI. That out of the $20,000,000 nitrate supply appropriation $100,000 be allotted for active investigation of processes for the industrial production of nitrogen compounds useful in the manufacture of explosives or fertilizers—this under supervision of the War Department.

VII. That in order to increase the production of ammonia and toluol the Government promote the installation of by-product coke ovens by directing priority in production and transportation of materials and parts.

VIII. That the decision as to more extensive installation of nitrogen-fixation processes and water-power development in connection with them be postponed until the plants above recommended are in operation or until further need arises.

IX. That while the preceding recommendations include all the measures that can now judiciously be taken for the fixation of ammonia, it is the opinion of the committee that the immediate accumulation and the permanent maintenance of an ample reserve not less than 500,000 tons of Chile saltpeter is the measure most urgently necessary.

The Interdepartmental Board unanimously recommended to the President on July 7, 1917, that the first six of these recommendations be approved, and on July 13, 1917, the Secretary of War advised the Chief of Ordnance of the Army that the President had approved the recommendations of the Interdepartmental Board. The Secretary of War then, in directing the Chief of Ordnance to proceed to carry out these first six recommendations of the Nitrate Supply Committee, also announced that for the present the consideration of development of large water-power installations, which had been begun by the Interdepartmental Board, would be suspended.

The outstanding feature of this program for action was the construction of the synthetic ammonia plant, using the General Chemical Co.'s process.

During the month of April the General Chemical Co. submitted various estimates to show the cost of the manufacture of anhydrous ammonia by their process and also to show economies that could be anticipated when the process was perfected. Under date of April 20, 1917, this company submitted to the President its first tender, which was not accepted. This tender modified, and resubmitted under date of June 5, 1917, was accepted by the Secretary of War on behalf of the President on July 14, 1917.

The proposal as accepted granted to the Government of the United States the use of its processes and designs of apparatus for catalytically combining nitrogen and hydrogen and other processes, patented or otherwise, upon the following terms: No royalties if products were to be used for munitions of war, and a royalty of $5 for each ton of 2,000 pounds of fixed nitrogen if products were to be used for fertilizer. No license was conveyed for use of the processes for other classes of material.

The General Chemical Co. placed at the disposal of the President the entire services of those members of its staff under whose supervision the process had been developed and agreed to communicate to the Government all of its knowledge and discoveries pertaining to the process. The Government was, on its part, to give information to the General Chemical Co., the wording of the clause being as follows:

> And, reciprocally, it is understood that all modifications and improvements in the processes or apparatus which the Government shall discover or employ shall be at the disposal of the General Chemical Co. and its licensees, if any, for use in its or their own works, and that all such modifications and improvements shall be freely exhibited upon request to the representatives of the General Chemical Co.

Previous to this approval, acceptance of tender, etc., by the Secretary of War, the Ordnance Department had been engaged in vigorous reconnaissance of that portion of the country recommended by the Nitrate Supply Committee, viz, the western end of the State of Virginia and contiguous territory, and in such studies of processes and of the engineering problems connected with the plant as was possible at the time. An engineering study of the General Chemical Co.'s process, of its design of apparatus for carrying out its processes, and of the buildings which it had planned for housing that apparatus was diligently carried on.

However, due to the approval of the President of the recommendations of the Nitrate Supply Committee and the acceptance of the General Chemical Co.'s proposal, the investigating and study stage of the project was passed, and on July 21, 1917, a separate division of the Ordnance Department, called the Nitrate Division, was created, to have charge of nitrogen fixation problems, with Col. J. W. Joyes, Ordnance Department, United States Army, as chief.

B. NITRATE DIVISION, ARMY ORDNANCE.

The Nitrate Division, also known as Division T, had, as its first duty, to carry out the recommendations of the Nitrate Supply Committee, for the execution of which further provision had been made in the tender of the General Chemical Co.

Plans for the location and construction of the synthetic ammonia plant naturally absorbed the energies of the new division for the first few weeks and left little time for investigating the process. These, however, had been already favorably reported upon by the Nitrate Supply Committee and orders for construction of the plant were mandatory, so that every effort was bent toward carrying out the program with the assumption that expectations with regard to the processes would be fulfilled.

This modified Haber process had been carried by the General Chemical Co. to the point where, having operating units upon something more than a laboratory scale, that company had felt sufficiently convinced of the value of the process to undertake the construction of a plant to cost about $1,000,000. Doctor Parsons, chief chemist of the Bureau of Mines, after visiting the General Chemical Co.'s experimental plant and after studying the plans for their modified Haber synthetic ammonia plant (of 7½ tons ammonia per day capacity) to be built at Shadyside, N. Y., advocated very strongly this acceptance of the General Chemical Co.'s proposal.

An understanding was reached with the General Chemical Co. whereby all the orders which they had placed for apparatus, building material—a very considerable proportion of which was required for the plant they had expected to build—should be transferred to the United States, which would thereby acquire all such apparatus at absolute cost of the same material to the General Chemical Co. and

with the advantage of a very considerable amount of progress, since some of these orders were placed as early as November, 1916. The contract with the General Chemical Co., covering these transactions, while dated as late as September 20, 1917, was made retroactive and covered assistance of this nature by that company from the date of the instructions of the Secretary of War, July 13, 1917.

1. United States Nitrate Plant No. 1.

In the meantime, on August 18, 1917, the J. G. White Engineering Corporation, 43 Exchange Place, New York City, was engaged to undertake for the Government the engineering and construction work for the General Chemical Co.'s process plant, which was now designated as United States Nitrate Plant No. 1. This contract, which was made retroactive to August 18, 1917, although dated as late as October 2, 1917, was upon the cost-plus percentage basis, as the work was not sufficiently clearly defined, and too much time would have been lost by attempting to so define it that a fixed price could be determined upon. In view of the very considerable amount of engineering which was to be done, it was considered that a fee of 9 per cent upon the actual cost of the work done, including the power-plant machinery but not the process machinery, was an altogether fair one. This engineering corporation rendered such services as to give complete satisfaction, and the officers and employees were not only competent, energetic, and loyal, but went out of their way to assist in every way possible in the work.

As a result of the long-continued and thorough examination of sites there was submitted to the Secretary of War on September 20, 1917, a report listing and giving the characteristics of nine sites which appeared to be worthy of serious consideration. Four of these—Chattanooga, Knoxville, Sheffield, and North Birmingham—had such advantages, however, as to be indicated as the places between which the ultimate choice should lie. On September 28, 1917, the Secretary of War advised that the President had decided upon Sheffield as the site upon which plant No. 1 should be built.

This site is located in Colbert County, in the northwestern corner of Alabama. The reservation, which finally totaled 1,900 acres, is a rolling land immediately west of the city of Sheffield, extending about a mile along the south bank of the Tennessee River and south to the Southern Railway, including at its easterly end the 100-acre property and idle buildings of a pipe foundry.

The main buildings of the new plant were located in the pipe-foundry area and the old buildings utilized as far as possible in the new plant.

In securing title for the Government to the various parcels of property comprising this site, Col. J. W. Joyes, Chief of the Nitrate

Division, represented that instead of having the land purchased by Government agents the citizens of the community select a committee to act as liaison between the Government and the landowners, with a view to securing the desired site at a reasonable price. At a public mass meeting 13 residents of Sheffield and Tuscumbia were selected to membership of that committee. There were also named three Government appraisers. The committee secured options from landowners and submitted these options to the Government appraisers. If the option secured met with the approval of the appraisers, the land was accepted. Donations were made of some 750 lots, and other lots were secured for about half their value.

On October 4, 1917, the first field party arrived at Sheffield and began the survey of the site. On October 9 the construction superintendent for the J. G. White Engineering Corporation arrived. Work began shortly after his arrival, the remodeling of the old foundry buildings receiving first attention.

The first building material, 3 cars of sand, arrived October 19, 1917, while on October 25 the first car of construction equipment was spotted. On the 26th work was begun on tearing down the old machine shop, and the smaller foundry accessory buildings were removed and the ground cleared for the site of the process building. The first concrete for permanent construction was poured November 9, 1917.

By the 1st of January, 1918, the machine-shop steel had been removed and reerected and concrete footings were in for the process building, power house, gas house, and gas holders, and a large amount of temporary work, such as roads, tracks, and material storage sheds, was under way.

At the outset of the work it was seen that the location of the plant was not favorable for workers, as the total population of the three near-by towns—Sheffield, Tuscumbia, and Florence—was not over 15,000. The working forces had been recruited to but 225 men when the local labor supply was exhausted, making necessary the recruiting by labor agents of outside labor, which brought in the question of housing and feeding.

Accordingly a site was selected for a white camp about three-quarters of a mile west of the factory area. Here work was started December 8, 1917, on the construction of a mess hall seating 950, 26 bunk houses accommodating 768, and 27 cottages, which were occupied January 9, 1918.

A negro camp, which consisted of 82 two-room houses accommodating 325 laborers, was started November 30 and bunks occupied December 19, 1917.

In the meantime, about August 14, 1917, Colonel Joyes, together with a member of his staff, visited the experimental plant of the

General Chemical Co. at Laurel Hill, Long Island, in company with the inventor of the process. The impression gained by this visit was rather unfavorable, and arrangements were made whereby several junior Army officers—chemists and chemical engineers—were detailed to the experimental plant for the purpose of making a careful study of the operation of the process. This study disclosed that while the process had great possibilities it would be necessary, in planning for additional nitrogen plants, to refrain from installing further plans on this process because the Ordnance Department could not feel assured of certainty of production within the time required. This uncertainty arose partly upon the difficulty of procurement of apparatus and partly upon lack of definite recorded operating data, upon which the department could base justification of its relying on the process.

The ordering, inspecting, and expediting of the materials and equipment of this plant were carried out almost entirely by the Washington office of the Nitrate Division. Great difficulty was met in placing orders for the 12 large forged-steel cylinders, as there were in this country only two establishments equipped to hollow-forge cylinders of the large sizes required. These companies—the Bethlehem Steel Co. and the Midvale Steel & Ordnance Co.—were overcrowded with war orders for the Army, Navy, and the Emergency Fleet Corporation, which, although carrying the same priority rating—Class A-1—as the Nitrate Division orders, were placed at an earlier date and so received preference. All these cylinders were finally worked into the schedule of the Midvale Steel & Ordnance Co. The machining was done by the Bethlehem Foundry & Machine Co. and Pusey & Jones.

The original plan, which directed that a plant be built to try out the General Chemical Co.'s synthetic ammonia process, together with the development of a process for the oxidation of ammonia to nitric acid, and for concentration of nitric acid, did not provide for an outlet for the product. Of the total 60,000 pounds of ammonia per day, only 8,000 pounds were to be converted into nitric acid, and no plans were made for the disposition of the resulting 24,000 pounds of nitric acid or the remaining 52,000 pounds of ammonia.

Early in 1918, therefore, a plan was worked out for oxidizing a little over half of the ammonia and for combining the resulting acid with the remaining ammonia, producing about 125,000 pounds of ammonium nitrate per day, or probably 22,000 tons per annum. The nitric acid concentration plant was then to remain as a merely experimental adjunct.

The plant was completed according to this schedule, and in addition property was acquired in sufficient quantity to provide for expansions and extensions of the original plant and for the erection of smokeless powder, picric acid, T. N. T. plants, etc.

Under date of January 30, 1918, a contract was entered into by the Government with the Chemical Construction Co., of Charlotte, N. C., to design, erect, and build in the shortest practicable time a complete nitric acid recovery plant, embracing oxidation and concentration plants.

Although the contract was dated as late as January 30, the contractor had started active progress prior to this date, and on January 10 unloaded his first cars of materials. On January 29 the first concrete for the oxidation and absorption building was poured, and concrete work on the concentration building began 10 days later. The erection of the steelwork on these buildings commenced on April 11, 1918.

The buildings, although built under war conditions, were designed for the peace-time operation of the plant. Accordingly proper provision had to be made for housing the employees on the reservation. After careful consideration a site immediately west of the construction camp was selected, with the idea of utilizing the construction buildings as far as possible in the permanent scheme.

Mann & MacNeille, landscape architects, of New York City, who were retained by the Nitrate Division to work up a design for the permanent village and housing, submitted the first sketches of five-room cottages on April 24, and on May 11 construction work was begun.

Although the J. G. White Engineering Corporation began work on the village May 11, the contract, a supplemental agreement to the main contract, bore the date of May 29, 1918. On July 8 the first of these permanent houses was occupied.

In the meantime construction of the manufacturing plant had been progressing rapidly, and on June 4 the first fire under the power-house boilers was lighted, while on June 11 rotary No. 1 carried load, the power house thus delivering its first power less than four months after setting the first steel. The operating department took over operation on June 23, and all contractors' employees were out of the power house by June 26, 1918.

In the oxidation building the first ammonia was oxidized to nitrous oxide on July 1, while on July 15 the first nitric acid (50 per cent) was drawn off at the absorption tower and placed in the storage tank. Following this the operating department assumed charge of the process building unit No. 1 on August 28 and the first synthetic ammonia was turned out on September 16. On October 28 nitric acid was neutralized to ammonium nitrate liquor, and on November 12, one day after the signing of the armistice, the first ammonium nitrate was produced.

After the armistice the 8-hour day was put into effect and the construction force reduced to 200 men. By December 3 all village construction activities, houses, roads, and grading had been taken over by the Ordnance Department and were completed by January 1, 1919.

All construction and operation activities were definitely discontinued in January, 1919. Unit No. 1, of 15,000 pounds of anhydrous ammonia per day capacity, was the only unit entirely completed and upon which operation was attempted. Unit No. 2, a duplicate of No. 1, and Unit No. 3, of twice the capacity of Unit No. 1, were partially completed. Continuous operation was never realized and only a small amount of ammonia produced. Many of the difficulties of operation were overcome by changes in the process or the development of special apparatus, but others were such as to actually obstruct successful operation and to be beyond ready correction. These, however, it is believed, have been corrected in the redesign of the plant now practically completed by the Nitrate Division.

Although this plant was fundamentally a trial plant for the General Chemical Co.'s "synthetic ammonia process," to be financed from funds made available by the "nitrate supply" section of the national defense act, the extension of the concentration project and the addition of the plant for the production of ammonium nitrate made the plant one of national defense. The financing of the construction cost of this plant, therefore, was from "national security and defense" and "armament of fortifications," funds with but $53,369.43 of "nitrate supply" funds.

The total gross cost of construction was $12,887,841.31. Of this amount $1,597,978.26 was for the permanent village, $503,369.43 for lands, and $198,223.26 for land improvements, roads, walks, etc. Expenses incident to operation were $710,476.12.

As has been previously shown, the process as installed is for the manufacture of producer gas, which is then used in the production of synthetic ammonia, a part of which is oxidized to nitric acid and neutralized by the remaining ammonia to form ammonium nitrate in solution, which is then grained or crystallized.

The rated capacity of the plant is 4,800,000 cubic feet of producer gas per day to be generated in blue-gas generators. This gas then flows to gas holders, from which it is drawn to the ammonia process building, where by the aid of a catalytic material the carbon monoxide is converted to carbon dioxide. Steam and air are now introduced and the pressure raised to 1,450 pounds per square inch. By means of another catalytic material the resulting nitrogen and hydrogen is liquefied to anhydrous ammonia. The rated capacity of this part of the process is 60,000 pounds of anhydrous ammonia per day. About one-half of this ammonia is then oxidized in the presence of a platinum gauze catalyst to nitric acid, in a plant of 200,000 pounds of 50 per cent nitric acid per day capacity, while the other half is used to neutralize this nitric acid to form ammonium nitrate solution. Approximately 200,000 pounds of 56 per cent ammonium nitrate solution may be produced per day, which is evaporated and grained to the finished ammonium nitrate.

As was to be expected, difficulties were encountered and changes were found necessary at every stage of the ammonia process in the attempted operation of the plant. In the gas-production part of the system it is found advisable, in order to better control the composition of the mixture, to supply the nitrogen content by admitting air through a supplementary burner which projected its flame into the gas stream rather than by blowing air into the water-gas generators, as had originally been planned. This supplementary burner also served to raise the temperature sufficiently for the oxidation of carbon monoxide to carbon dioxide in the carbon monoxide converter, making unnecessary the superheating of the admixed steam as had been intended.

The water scrubbers and copper scrubber of the purification system were found to be inefficient, but their operation was improved by providing a better type of packing and by consolidating the scrubber cylinders to form towers of double height. The greatest difficulty, however, was experienced with the hot caustic system for removing the carbon monoxide, since it was found to be impossible to maintain tight pipe joints under the corrosive action and high pressure of the hot caustic. The difficulty was finally solved when it was found that the bulk of the carbon monoxide could practically as well be removed by the copper solution and the residual carbon dioxide by operating the caustic system cold.

Great difficulties also were experienced with the ammonia synthesis and liquefaction systems. The ammonia catalyst is contained in a steel bomb about 48 inches internal diameter and 15 feet 2 inches long, with screwed heads, top and bottom. The main difficulty was the inability to keep this bomb tight in view of the pressure of 1,450 pounds per square inch which had to be maintained. The catalyst operated at 500° C., which temperature was maintained by heat interchangers and a gas heater, which supplied additional heat at the entrance to the bomb. The tubes in the heater burned out frequently, permitting the escape of gas, which often caused the process to be shut down. The escaping hydrogen often ignited, but fortunately there was no loss of life in any of these accidents. Pipe joints also failed, due to excessive strains put on them by expansions and contractions caused by differential temperatures in the system. It had been planned to remove the product from the gas mixture as anhydrous ammonia, and a refrigerating system was installed for this purpose. The refrigerating plant, however, was found to be less than one-third the proper capacity, and it was necessary to install all the refrigerating equipment intended for the three units in order to liquefy the product of one.

Facilities were necessary for producing the catalysts required for the conversion of the carbon monoxide to carbon dioxide and for the conversion of the hydrogen-nitrogen mixture to ammonia, and also for the sodamide used in gas purification. A proposal of the General Chemical Co. that they erect a plant at one of their works and prepare this material at cost was accepted September 8, 1917. Little difficulty was encountered in making the catalyst for the carbon monoxide conversion and the sodamide, but great difficulty was experienced in making catalyst for ammonia synthesis. Much concern was felt over this fact, inasmuch as this material is vital to the success of the process, and the Nitrate Division, in July, 1918, established, through the assistance of the Department of Agriculture, an experimental station at Arlington, Va., for the study of the production of this catalyst. The best scientific talent available was called in, but due to the lack of time satisfactory results were not obtained. The problem was later turned over to the Fixed Nitrogen Research Laboratory established at the American University, the work of which is discussed elsewhere in this publication.

Since according to the "nitrate supply" act the product of this plant was to be not only for munitions of war but also "useful in the manufacture of fertilizers" as well, and as the plant did not function properly, the problem of redesign was one of immediate interest. On July 29, 1920, there was formed a "plant 1 section" of the Nitrate Division for the redesign and modification of the ammonia process of United States Nitrate Plant No. 1, with Mr. R. S. Tour in charge. Mr. Tour had been chief of the technical department at the Sheffield plant and had also been a member of the nitrate commission which visited the atmospheric nitrogen fixation plants of Europe in the summer of 1919.

A program of action was mapped out, but for reasons stated below this program was only partially carried out. The program included: Laying out definite, although not detailed, plans for remodeling, reconstruction, or replacement of portions of the installation; engineering experimentation to obtain necessary data and to test certain mechanical devices; completed designs with all necessary details for construction and erection of United States Nitrate Plant No. 1; fabrication, construction, and erection of the developed designs and modifications; experimental operation of the modified unit at Sheffield, Ala., this to include such changes and modifications as developed during experimental operation.

It was planned that the entire program should be completed by July 1, 1923. Construction was to be started by the summer of 1921 and completed early in 1922, leaving about one year for trial operation and development. The cost estimate for this program, including the modification of unit No. 1, using the Haber-Bosch process, and the installation of an electrolytic hydrogen generating plant for trial of the Haber electrolytic process, was:

Modification:		
1. Gas production and purification	$243, 335	
2. Circulation and liquefaction	127, 814	
3. Auxiliary equipment	50, 000	
4. General expense	127, 065	
		$548, 214
Trial operation (7 months for the Haber-Bosch and 3 months for the Haber electrolytic system):		
1. Labor	198, 530	
2. Materials and supplies:		
Power	160, 625	
General	115, 748	
		474, 903
Total		1, 023, 117

In view, however, of the construction and erection of a synthetic ammonia plant at Syracuse, N. Y., by the Atmospheric Nitrogen Corporation, it was deemed inadvisable for the Government to continue experimental work at Sheffield, and the Chief of the Nitrate Division recommended to the Chief of Ordnance on March 24, 1921, that the reconstruction of United States Nitrate Plant No. 1 be deferred and the plant be retained in the most economical stand-by condition. This recommendation was concurred in by the Chief of Ordnance and was approved by the President on April 30, 1921. Accordingly, the first three items only of the original program of redesign have been carried out.

In connection with this redesign, outside engineering advice was sought whenever possible and wherever available. The general considerations in the redesign were: Changes found by experience in the operation of the Sheffield plant to be absolutely necessary before operation could be attempted; changes indicated by general engineering practice to be fundamentally necessary before successful operation could be hoped for; basic changes in the process, especially the substitution of electrolytic production of hydrogen for the present method and apparatus installed.

The designs were based on considerations of economy from the standpoint of the utilization of available equipment; certainty of operation; simplicity of construction; small experimental investment; ease of later modification to large capacity.

General layouts of the remodeled plant and general drawings of the various items have been completed, covering in addition to the changes which were made tentatively during the former trial operation such improvements as modifications of the water, caustic and copper scrubbers, a new type of liquid level control, a continuous type of copper solution regenerator, a new high-pressure stop valve for use on the hot lines, a new design of heat interchanger, and a new design of ammonia converter. A number of mechanical investigations, descriptions of which are given under "Miscellaneous mechanical investigation," Chapter VI, were made for the determination and solution of various design problems. The drawings and reports on investigations are on file in the War Department and will be available as a basis for complete detail drawings in case it is ever decided to proceed with the reconstruction part of the program.

The plant has since January, 1919, been maintained in idle stand-by condition by a small force of painters and mechanics and is rigidly inspected semiannually by a consulting mechanical engineer in private practice.

2. United States Nitrate Plant No. 2.

The construction and erection of United States Nitrate Plant No. 1 constituted a compliance with the instructions of the Secretary of War, but the Ordnance Department did not confine itself to this limited program. The Nitrate Division worked ahead to the increasing need for service to relieve the drain upon the shipping resources of the country in the importation of nitrate and to remedy for the serious emergency which would occur should importation be entirely cut off, as by submarines or by interference in Chile itself. There was, therefore, intensive search for processes which could be installed, whenever the need should become sufficiently urgent, with the least delay and with a greater certainty of production within a stipulated time than could be expected from the General Chemical Co.'s process until actual experience therewith could have demonstrated its capabilities.

In such a survey of the field of possibilities, the Nitrate Division was inevitably led to the recognition of the fact that the only process then operated on this continent as an actual going concern was that of the American Cyanamid Co.

When, therefore, in October, 1917, the Ordnance Department was confronted with the very large deficiency of supply of explosives and of materials for explosives, below the estimated requirements, and the Gun Division of the Ordnance Office, on October 24, 1917, notified the Nitrate Division of the urgent need of a further supply of ammonia, the Nitrate Division proposed to help by using the American Cyanamid Co., to produce the high explosive, ammonium nitrate, without requiring either ammonia from any outside source or sodium nitrate from the only possible source, Chile.

The American Cyanamid Co.'s earlier tentative proposals were based upon the theory of the plant being built by the company at the expense of the United States, but with no payment whatever to the company as profit, the emolument to be the complete transfer of all right and title to the plant, after the war use thereof, to the American Cyanamid Co. These propositions, however, were not favorably received. One of the proposals, dated October 29, 1917, also contained an offer to operate to capacity their then existing plants for the production of ammonia to be sold exclusively to the Ordnance Department. This part of the proposal was accepted, and through the use of this ammonia, purchased in the form of aqua ammonia, fixed atmospheric nitrogen did find its way into American explosives.

The need for the high-explosive ammonium nitrate was urgent; no adequate supply of the ammonia needed as its base existed, or could be created, except by the cyanamide process. The other constituent, nitric acid, could only be made from Chilean nitrate or by the cyanamide process. There was scant production of nitrate in Chile and shortage of ships to import it; there was great and unmeasurable danger of interruption of production in Chile by German plots and of interruption of importation by German submarines and by German damage to the Panama Canal. The American Cyanamid Co. not only had a monopoly of the patent rights for the cyanamide process, but had a strong strategical position in the negotiations because of their experience in the actual use of this process, which no other corporation on the American continent, at that time, had.

Discussion on these various proposals was entered into generally by the Chief of Ordnance, president of the American Cyanamid Co., Mr. Baruch, and others of the War Industries Board, and several officers of the Ordnance Department.

After the rejection of the proposal of October 29, previously mentioned, several other proposals were considered and rejected. Each offer, however, came nearer to being acceptable to the Government than its predecessor, until on November 13, 1917, an offer was submitted which, although not entirely satisfactory, was considered the best compromise which could be made and was accepted by the Government upon the approval of the War Industries Board.

The final contract, which bears the date of November 16, 1917, was duly signed December 4, 1917.

This accepted tender proposed that whereas the American Cyanamid Co. being unwilling to risk its assets would create a subsidiary company, Air Nitrates Corporation, and would give that company full assistance, knowledge, good will, and license to patented process, all for 6 mills per pound of nitrogen, equivalent to one-fourth cent per pound of ammonium nitrate; Air Nitrates Corporation to receive for designing, constructing, etc., 3⅓ per cent of the cost of the plant, estimated at $30,300,000, with a maximum limit of this fee of $1,000,000; Air Nitrates Corporation also to receive one-fourth cent per pound of ammonium nitrate as manufacturing fee.

At the same time as these negotiations were taking place, the Cyanamid Co., at the instance of the Government, was investigating the large engineering and construction companies of the country to find that company best fitted to construct and erect the proposed plant. It was found that Westinghouse, Church, Kerr & Co. of New York, engineers and builders, who had done considerable work on the American Cyanamid Co.'s Niagara Falls (Canada) plant, were completing a large job and so had the necessary construction personnel and equipment to immediately transfer to this new project. It further developed that the J. G. White Engineering Corporation was in a position to start construction of the steam power plant at once.

On November 17, 1917, therefore, the day following the date of the contract between the Government and the American Cynamid Co. and the Air Nitrates Corporation, the Air Nitrates Corporation entered into contracts with Westinghouse, Church, Kerr & Co. and the J. G. White Engineering Corporation.

The contract with the Westinghouse, Church, Kerr & Co. called for the subcontractor to, "in the shortest time possible, do the necessary engineering involved in the designing, drafting, and laying out of the work based on the general drawings, specifications, and directions furnished by the corporation from time to time, and furnish labor, materials, tools, machinery, equipment, facilities, and supplies, and do all things necessary in the construction and completion of grading, drainage, sewerage, and water system, buildings, foundations, roads, and ways; such machinery and equipment, if any, as the corporation may request the contractor to furnish and install; and such other work at the site of the general plant or distant therefrom, but related thereto, as the corporation may specifically request in writing."

As compensation the contractor was to receive 6 per cent of the total cost of the work except that of 5 per cent on the total cost of work done by the subcontractors.

The J. G. White Engineering Corporation contract called for the subcontractors to do the necessary engineering involved in the designing, drafting, and laying out of the work based on the general drawings, specifications, and directions furnished by the corporation from time to time, and furnish labor, material, tools, machinery, equipment, facilities, and such supplies, and do all things necessary for the construction and completion of a steam-electric power plant of substantially 55,000 kv.-a. capacity, together with its appurtenances, such as coal storage, ash removal, and intake.

The compensation, as in the case of the contract with Westinghouse, Church, Kerr & Co., was to be 6 per cent of the total cost of the work except that of 5 per cent on the total cost of work done by subcontractors.

Although operation of the proposed nitrate plant would require approximately 90,000 kilowatts of power, and the power-plant housing was of sufficient size to accommodate electrical generating equipment of this capacity, but 60,000-kilowatt capacity equipment was to be installed here at this time. It was decided that the remaining 30,000 kilowatts could be secured at an earlier date from the Alabama Power Co., which company at that time owned and operated an electric generating, transmitting, and distributing system in north Alabama, which included, in general, a hydroelectric plant on the Coosa River with an installed capacity of 67,500 kv.-a.; a transmission network (including a 110,000-volt system) connecting this plant with various other plants and substations; a steam reserve generating plant known as the Warrior station, on the Black Warrior River, having an installed capacity of 25,000 kv.-a.; and certain rights of way extending approximately 20 miles from the Warrior station toward Sheffield.

Although this plan met with opposition from the main contractor, who contended that the whole 90,000-kilowatt capacity should be installed at the plant site, the wisdom of the Government's decision was well brought out when in October, 1918, a portion of the plant was ready to start up, the river power house was not nearly ready to supply the necessary power, which was supplied by the Alabama Power Co.

Under date of December 1, 1917, an agreement was entered into by the Alabama Power Co. and the United States of America whereby the contractor, Alabama Power Co., was to, at its own cost and expense, supply all labor, materials, supplies, etc., and do all things necessary for installing between its 110,000-volt system and its Warrior substation a tie line and other facilities of capacity and character sufficient for transmitting continuously 30,000 kilowatts of 3-phase, 60-cycle, alternating current at 110,000 volts, to the Warrior substation and through it to the transmission line referred to below; to, at the expense of the United States, prepare designs and plans for and, upon their approval, construct and erect, as an extension to the contractor's Warrior River station, a new power station building with a 33,333 kv.-a. steam turbo generator with boilers and switchboard and other necessary facilities; a new Warrior substation and apparatus; a Muscle Shoals substation; and a Drifton extension railroad to connect the Drifton Branch of the Southern Railway with the Warrior extension, a distance of 8,000 feet; to survey and secure title to, at the contractor's expense, the necessary right of way approximately 100 feet wide to provide, in conjunction with its present right of way of 20 miles length and 100 feet width, a continuous and reasonably direct right of way for a transmission line from the Warrior substation to the United States Nitrate Plant No. 2, Muscle Shoals, and to, at the expense of the United States, design, construct, and erect a transmission line on this right of way and connecting the Warrior substation with the Muscle Shoals plant, of capacity and character sufficient for transmitting continuously 30,000 kilowatts of 3-phase, 60-cycle, alternating current of 110,000 volts. The contractor to receive, upon the signing and delivery of the contract, for use of his lands and other facilities by the United States, and in lieu of overhead, the sum of $60,000, in addition to a fee equal to 6 per cent of the cost of construction and equipment performed or supplied by the contractor. The United States was further to pay the contractor 6½ mills per kilowatt hour of energy actually delivered to the United States at the Warrior substation.

On November 22, 1917, less than a week later than the date of the contract for the construction of the plant by the Air Nitrate Corporation and the date of the principal subcontracts, a party representing the Government, the main contractor, and the two principal subcontractors arrived at Sheffield to inspect the site at Muscle Shoals, which had previously been suggested by the American Cyanamid Co. and approved by the Government.

This party went over the site and definitely laid out by indication the various buildings of the manufacturing plant, including the 60,000 kilowatt steam electric power plant in the ravine along the edge of the Tennessee River.

The cyanamide process, as shown in a previous chapter in more detail, is one of nitrifying finely ground calcium carbide heated to incandescence by carbon electrodes in an oven; the resulting calcium cyanamide is then finely ground and autoclaved, liberating ammonia gas.

At the United States Nitrate Plant No. 2 the raw materials, limestone and coal, are brought in at the north end of the manufacturing plant, the process proceeding in a southerly direction.

Limestone burned in a battery of coal-fired kilns forms a lime, which is mixed with dried, finely powdered coke, and fed to the large carbide furnaces in the next group. This mixture is heated to a molten mass by the use of large carbon electrodes and the resulting calcium carbide tapped off, cooled, crushed, and ground, and fed to the lime nitrogen ovens. Here the carbide is highly heated in the presence of nitrogen, which is readily absorbed. The resulting pigs of calcium cyanamide are ground and the resulting powdered material hydrated to destroy as far as possible any free calcium carbide. This, then, is treated in the ammonia gas group with high-pressure steam in steel cylinders and ammonia gas liberated. As in the case of plant No. 1, a portion of this ammonia gas is then oxidized to nitric acid in a converter using a platinum gauze catalyst, and the resulting nitric acid neutralized with the remaining ammonia gas to form ammonium nitrate solution, which in turn is crystallized out to grained ammonium nitrate.

The nitrogen is supplied by a large installation of Claude nitrogen columns, located in a plant to the east of the lime-nitrogen oven group.

The rated daily capacities of these various groups in the manufacture of ammonium nitrate are: Calcium carbide, 475 tons; lime nitrogen, 600 tons; ammonia gas, 150 tons; nitric acid, 260 tons; and ammonium nitrate, 300 tons.

The terrain of the plant proper site, which was mostly a cotton field, was fairly level, while the site selected for the village, although not unduly rough or hilly, was rather undulated and was likewise a cotton field, intermingled with patches of timber.

One of the important ends sought and believed to be obtained in the location of United States Nitrate Plant No. 2 at the Muscle Shoals site was sufficient available and potential power. The Alabama Power Co.'s system and the possibilities of the tremendous power development in the Tennessee River at this point met these requirements.

In securing title to the 2,306 acres comprising the plant site, the committee of citizens of the community, as in the case of United States Nitrate Plant No. 1, secured options to the various parcels and turned these options over to the Government for examination and purchase of the property.

The Southern Railway was engaged by the Air Nitrates Corporation to make the rail connections to the plant site and to place both permanent and temporary track according to plans and directions as given from time to time. On November 23, and therefore the day following this first visit to the site, the Southern Railway engineers first started work, staking out the line. By December 10, 1917, rail connections had been made to the main line and run far enough into the plant site to unload the first construction material to arrive. This material was consigned to the Southern Railway. The first construction material for the Westinghouse, Church, Kerr & Co. arrived December 19, 1917, while the first car for the J. G. White Engineering Corporation was spotted January 15, 1918.

In the meantime the Chemical Construction Co. had been engaged by the Air Nitrates Corporation, according to the terms of the contract dated February 1, 1918, to design, erect, and build a complete nitric acid recovery plant consisting of 12 units, each unit to have a capacity sufficient to treat 2,500 cubic feet per minute of gas containing 8 per cent NO. This work was to include one gas cooling plant comprising gas flue connections, steam boilers, gas coolers, and oxidation towers; and a nitric acid gas absorption plant, with acid storage, weighing tanks, exhausters, and acid pumping equipment.

As compensation this subcontractor was to receive a fee equal to 8 per cent of the cost of the work, except that his fee was to be 5 per cent of that part of the work of his contract performed by subcontractors. The maximum compensation was not to exceed $240,000.

The first construction material under this contract arrived at the site January 5, 1918.

The schedule of order of construction to be followed by the Westinghouse, Church, Kerr & Co. was: Railroad tracks to serve site; roads from Florence and Sheffield to be put in shape to stand traffic and reconstruct so-called River Road to provide access to plant; provide temporary office buildings; provide temporary water supply from spring located near river bank; provide camp and commissary, including water supply and sewer system, to house and feed workmen, also an emergency hospital; provide temporary utilities for light and power, water supply, compressed air, steam, machine shop, garage, etc.; construct manufacturing plant with its utilities; construct an industrial village with all its utilities to house the permanent operatives.

In following out this schedule, therefore, March 1, 1918, found the amount of permanent construction, with the exception of the railroad yards built by the Southern Railway, practically nil. Then, too, the severe winter, which was without precedent for that section of the country, the thermometer registering as low as 8° F., materially slowed up all work.

Construction of the cantonment started on December 29, 1917, and by February 23, 1918, had reached a capacity of 7,664 workmen; May 11, a capacity of 11,630; and by September 1, 15,403. A girls' dormitory of a capacity of 192 was completed July 6.

All these buildings were frame, with one-ply tar paper covering. In addition to these there were three tent colonies of a total capacity of 344.

As the total number of male employees on the whole job reached the peak of 19,263 on August 8, 1918, and as the neighboring towns had but extremely small amount of surplus housing capacity, the dire need for these temporary quarters can be seen. In addition, accommodations had to be made for the families of a large number of this force, which brought the population of Muscle Shoals to over 25,000.

The temporary construction included 1,376 temporary buildings for housing, a temporary boiler plant having a capacity of 1,000 horsepower, a power house of 300 kilowatts capacity, with necessary distribution, three pumping stations and a distributing pumping station of a capacity of 2,000,000 gallons of water per day, a compressed-air plant, machine shop, carpenter shop, sheet-metal shop, and a garage maintaining and operating at one time 75 automobiles and 43 trucks.

The first permanent work started was by the J. G. White Engineering Corporation on the power house during the end of January, 1918. That corporation's representative at the outset arranged to do the work by using the minimum number of men. To this end he made plans the first thing for all the necessary labor-saving machinery possible, and the work started off excellently.

While the months of January and February were extremely poor for construction, ideal weather prevailed during the spring, and the first rainstorm heavy enough to stop work since early in March occurred on May 5. Very material progress was made during this time.

Building and equipment foundations had progressed so favorably since the breaking of ground for the first permanent manufacturing building in February that the installation of the permanent manufacturing equipment started on April 30 in the nitric acid building. This was closely followed by the limekilns and equipment, installation of which was started on May 5, and following in rapid succession the autoclave and process boiler house equipment on May 13, the liquid air on May 21, the lime-nitrogen mill on May 23, and so on, until the end of August found installation of equipment progressing in all divisions of the process.

By the latter part of October, 1918, such progress had been made as to warrant operation of the plant at one-fifth capacity. Construction had been so carried out as to render a complete line through the whole plant available for operation at once.

In the meantime, while construction of the river power house was progressing as swiftly as could be expected under the circumstances, greater trouble than had been anticipated was experienced in getting down to solid bedrock for foundations, causing a much larger quantity of excavation than had been estimated and so delaying the date of availability of power. It was early seen that the plant could not be operated before several months after its readiness for starting up on power from this station.

However, although work on the Warrior extension was not progressing with the hoped-for speed, the 89-mile transmission line started in January, 1918, was completed on May 23, 1918, eight days before scheduled time and assured starting up power. Some delay to the Warrior extension was caused by the inability of the electrical committee of the War Industries Board to immediately "clear" the required turbo-generator, while the largest factor was labor conditions, weather conditions, and engineering and construction miscalculations.

By the 1st of August, 1918, construction of the turbo-generator foundations was practically completed and the General Electric Co.'s erector arrived on the job August 5 for the purpose of superintending the erection and tuning up of the 30,000 kilowatt turbo-generator. Erection of this generator started on August 16 and proceeded through the rest of that month, the month of September, and up to October 20, when it was ready to be turned over.

On September 25 the boiler house was fired, and by October 5 six boilers had been put to use.

On October 27 the turbine was ready for steam to be furnished, but due to inability to secure and hold the necessary vacuum it was not until November 14 that the turbine was actually turned over, and then for only 10 minutes, transformer trouble causing the shutdown. From this time until December 29 numerous attempts at operation were made without satisfactory results. However, between December 29 and January 3, 1919, inclusive, the turbine operated satisfactorily with a load of up to 30,000 kilowatts, and between January 11 and February 1, 1919, the first Government boiler house and turbine were operated to supply power for the test run of United States Nitrate Plant No. 2.

While this was in progress, the Air Nitrates Corporation was ready for and received 2,000-kilowatt service at 44,000 volts over the newly completed transmission line on July 1, 1918, with continuous service from then on for construction and operating purposes.

Practically indispensable aid was rendered by the various committees of the War Industries Board in securing the necessary materials and equipment for the plant. This included, among numerous other materials, cement, lumber, steel, all manner of electrical and steam-generating equipment, locomotive cranes, acid-proof iron, copper bus bars, copper and brass tubing, etc.

For operation, allocation of contracts for the necessary supply of coal and coke were made through the Fuel Administration, which agency was not only instrumental in effecting these contracts but also assumed responsibility for their fulfillment.

The other raw material required for operation was limestone crushed to 1½ to 2 inches. To secure this material, the Air Nitrates

Corporation entered into a contract, dated January 16, 1918, with Foster & Creighton, operators of Rockwood quarry, a limestone quarry and crushing plant about 26 miles distant. There was being installed at this quarry an additional crushing and screening plant.

In the latter part of March, 1918, however, it became apparent that a better and more certain source of limestone must be found. Accordingly investigation of the northwestern part of Alabama, south of the Tennessee River, was undertaken, with the result that a site known as Hill property, later called Waco quarry, 6 miles east of Russellville, Ala., was selected as best filling all conditions.

In the meantime the Air Nitrate Corporation had stationed a quarry engineer at Rockwood to aid in the production of stone which began on July 1, 1918. Delivery was to be made at the rate of 500 tons per day from July 1 to December 31, 1918, and 1,000 tons per day starting January 1, 1919.

It became apparent during the first two weeks of operation, however, that the plant and equipment installed was totally inadequate and would not even approximate this tonnage. Accordingly, the quarry was taken over by the Government upon the approval of the War Industrial Board, and additional equipment installed. In this way, although the amount of stone contracted for was not delivered, a sufficient supply for operation and reserve was on hand at the time of the deferred starting up of the plant to insure no interruption.

The Waco quarry site was now being actively prospected and orders placed for the necessary equipment. Actual purchase of the parcels of land making up the 440 acres of this site was not started, however, until after the authorization by the Assistant Secretary of War on January 4, 1919. The equipment previously ordered was placed in storage at Muscle Shoals.

The actual operation of the nitrate plant may be said to have commenced at the time the electric current was first turned on in the carbide furnaces, which took place at 12.02 p. m., October 26, 1918. On October 23, 1918, the first air compressor was started in the liquid-air plant. The first nitric acid was produced at 1.30 a. m., November 19, 1918, and the first ammonium nitrate at 3.20 a. m., November 25. Thus one month elapsed from the beginning of the carbide manufacture to the time of production of the finished ammonium nitrate, and the first ammonium nitrate was produced just two weeks after the signing of the armistice.

The finished product, ammonium nitrate, met all of the specifications of the Inspection Division. This, together with the manner in which each step in the process was carried out, was a great satisfaction, as it justified the judgment of the Government in the selection of the process for the production of ammonium nitrate for war purposes at least.

The signing of the armistice removed the pressing need for ammonium nitrate for war purposes. Accordingly a conference was held in the office of the Assistant Secretary of War on November 19, 1918, to determine upon a program to be followed in connection with the United States nitrate plants.

At this conference it was decided that plant No. 2 was to be completed and to be operated sufficiently to demonstrate its capacity and efficiency. Additional expenditures at the plant of an investment character were to be limited to facilities required for the plant solely in connection with its use for war purposes. This was included in a memorandum signed by the Assistant Secretary of War, Director of Munitions, on December 2, 1918.

Construction therefore continued, but with reduced forces limited to the conditions of the 8-hour law and the avoidance of overtime. This condition delayed the completion of the plant to the late spring or summer of 1919.

The completed plant comprised 306 permanent buildings, of 29 acres of ground space, and 1,387 temporary buildings, of 46 acres. The materials for these buildings and their contained equipment were unloaded from over 18,000 freight cars, which contained, among other materials, 12,000 tons structural steel, 250,000 barrels cement, 45,700,000 board feet of lumber, and 5,000,000 brick.

The test to demonstrate the capacity and efficiency of the plant by operating two complete lines (one-fifth plant capacity) was started midnight of January 11, 1919. Each department of the process was given a two weeks' run by the Air Nitrates Corporation under the direct supervision of the Government force stationed there.

In general the several departments of the plant performed their functions satisfactorily. It was to be expected that in a plant of such magnitude, and especially in one in which processes are employed that have never before been used on a commercial scale in this country, it would be found that certain alterations and improvements would be necessary. But even these were few and none such as would cause cessation of operations.

The apparatus and equipment was found to have a capacity equal to and in many cases in excess of its requirements.

In all there was produced some 2.200 tons of lime nitrogen remaining as such and 1,700 tons of ammonium nitrate.

At the completion of this test preparations were made for maintaining the plant in indefinite idle stand-by. All equipment was cleaned of its accumulation of materials of operation; bearings and shafts were heavily greased; water lines broken at the various pieces of equipment to insure dryness; destructable gaskets removed; elevator chains painted with heavy oil; belts removed, coated with neat's-foot oil or powder, as their nature required, rolled, and stored, etc.

Power for this test was supplied by the Government's Warrior extension, through the transmission line, as the river power plant was still under construction.

Progress on the river power house generating station was also curtailed by the reduction in force and 8-hour law, and was not ready for full operation until August, 1919.

Beginning September 10, 1919, and continuing until October 30, 1919, the complete station, excepting the low-pressure east turbine (which early developed a rubbing between blades and blade rings), was operated under varying conditions of load up to 33,000 kilowatts, the capacity of the Warrior-Muscle Shoals transmission line, over which energy was delivered to the Alabama Power Co.'s system.

The results obtained during the period indicated that the manufacturers had fulfilled their guaranties of operating efficiencies, but that improvement was necessary in the construction of the low-pressure turbine to eliminate the danger of contact and rubbing between revolving and stationary parts.

Following the completion of this test run the Westinghouse Electric & Manufacturing Co., which furnished and installed the main turbine unit, rebuilt the two low-pressure rotors which form parts of it, refitted the stationary blade rings, and after exhaustive check measurements, all at the expense of the company, placed the turbine in condition for operation and further test.

On June 22, 1920, a contract was entered into with the J. G. White Engineering Corporation by the United States under which that corporation undertook to supply all labor, fuel, miscellaneous supplies, etc., and conduct the test of the reassembled turbo-generator.

The J. G. White Engineering Corporation in turn entered into a contract with the Westinghouse Electric & Manufacturing Co., dated June 22, 1920, under which the latter agreed to furnish the specially trained personnel required to condition and operate the turbo-generator, its auxiliaries, etc., and the necessary superintendence.

The first boiler was fired on July 20, 1920, and steam supplied for the operation of both of the 2,500-kv.-a. house turbines on July 23. The remaining 11 boilers were successively conditioned and fired as required.

The plant was regularly put into operation October 1, 1920, and the supply of energy to the Alabama Power Co., with which company arrangements had been made to purchase the power generated, commenced at 11 p. m. that date.

Operation continued up to and including November 8, 1920, during which time a total of 9,170,170 kilowatt hours of power was sold to the Alabama Power Co.

The sole object of the test was to demonstrate the effectiveness of the repairs and adjustments to the 60,000 kilowatt turbogenerator by subjecting the turbine to such operating conditions as are usually encountered in the commercial operation of large central stations. All other main features of the plant had been satisfactorily proven out during the test run in the fall of 1919.

The maximum load carried during the test was 33,000 kilowatts, which maximum was governed solely, as in the case of the previous test run, by the capacity of the Muscle Shoals substation and the 89-mile 110,000-volt transmission line to Gorgas, where the Alabama Power Co. distributed the energy purchased by it.

It was not possible, therefore, to load the turbine unit to its rated and overload capacities of 60,000 kilowatts and 70,000 kilowatts, respectively, but the satisfactory results obtained during single and combined operation of the individual elements indicated clearly that no fears need be entertained for the equally satisfactory operation of the unit as a whole and under the full and overload conditions specified in the contract.

The total gross cost of these projects known as United States Nitrate Plant No. 2 was $75,181,528.41, made up of $69,022,669.20 for Plant No 2 proper; $4.979,782.22 for the Warrior River station, transmission line, and substations; and $1,179,076.88 for the Waco quarry.

Of the $69,000.000 for Plant No. 2 proper, $51.894,360.31 was for the permanent manufacturing buildings, including $12.627,103.80 for the river power house; industrial village and permanent quarters, $2,753,014.91; auxiliaries, such as roads and walks, sewers, water system, and reservoir, railways, trolley line, fencing, telephone, etc., $5,006,044.35; the remainder being expended for temporary quarters and facilities and miscellaneous items.

The Warrior River project expenditures were made up of $3,417,702.70 for the Warrior generating plant, $573,600.34 for the Warrior and Muscle Shoals substations, $938.057.35 for the transmission line, and $50,421.94 for the Drifton Branch Railroad.

During the spring and summer of 1919 the report of the operating test of the plant conducted during January, 1919, was given serious study. Where operation had not proceeded smoothly tentative redesigns or rearrangements were laid out, such as would render United States Nitrate Plant No. 2 effective as a military establishment.

Prospecting of the Waco quarry was also continued, and a quarry and crushing plant tentatively laid out and designed.

Estimates for the cost of making these corrections and additions and constructing the quarry totaled $1,250,000. On November 1, 1919, Mr. Glasgow, who was leaving this country, recommended that $1,250,000 be appropriated to carry out this work. This recommendation was approved February 3, 1920, by the Secretary of War.

The commanding officer of plant No. 2 was now directed to immediately start work on a number of the minor corrections, including new drives for lime nitrogen silo conveyors, new autoclave acetylene outlets, gauges and agitators on certain tanks, provisions for removing dust from certain pieces of equipment, completion of some unfinished electrical work, construction of walkways at various pieces of equipment, etc.

General designs were also made up for the remaining work, which consisted of the installation of a new coal dryer, a coal conveyor to the coke dryer, and installation of other mechanical equipment, the raising of the raw-material unloading and storage trestle to an elevation 10 feet higher, the construction and erection of an ash-disposal system for each of the river power plant and process steam plant, construction of roads and a drainage system, and the Waco quarry and crushing plant.

These designs were then submitted to the construction service of the office of the Quartermaster General, which service got out detailed drawings, wrote up specifications, let contracts, and supervised the carrying out of the terms of the contracts. All contracts had been awarded by June 30, 1920, and work started at once.

The Waco quarry project was the largest single item of this work. Contract for the job was awarded to the Arthur G. McKee Co., of Cleveland, Ohio, at a final contract price of $533,006.60. However, as previously noted, much of the equipment had been purchased during the year 1918 and at the signing of the armistice stored at United States Nitrate Plant No. 2. This makes the total cost to the Government for this quarry and crushing plant of 2,000 tons crushed limestone per day capacity $1,179,076.88.

At the completion of the job on June 14, 1921, the crushing plant was given an idle operating test, which proved to be very successful. The plant has been maintained in idle stand-by since.

With the return of the military and agricultural commissions from Europe in the late summer of 1919,[1] the investigations looking toward the future of plant No. 2 had reached conclusions which, under date of October 22, 1919, in a letter addressed to the Secretary of War by Mr. Glasgow, were interpreted into definite recommendations regarding the disposition of United States Nitrate Plant No. 2 at Muscle Shoals.

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[1] See VII, D, U. S. Fixed Nitrogen Commission, p. 310.

The war had demonstrated beyond dispute that no nation is safe which is dependent upon a foreign supply of nitrogen. The Government possessed the United States Nitrate Plant No. 2, a proven source of 40,000 tons per year of nitrogen fixed in the form of 110,000 tons of ammonium nitrate, but no longer had a demand for this product. The question of how to retain this emergency preparedness through peace times, therefore, was reduced to two considerations: One, the maintenance of the plant in idle stand-by; the other, the utilization of the plant for the commercial production of fertilizer materials.

To carry out the first scheme there would be required a small maintenance force continually going over the plant, the expense of which would be a dead loss to the Government. It was estimated that proper maintenance would require the expenditure of $200,000 per year, and that even with this expenditure the plant would gradually become obsolete.

While the commercial production of fertilizer would entail an initial investment for the installation of additional buildings and equipment, this would be rather small and would eventually not only save to the Government the cost of idle maintenance but would also be a source of income, and at the same time insure the readiness of the plant and a trained personnel for a war emergency.

Study showed that the plant would lend itself very readily to the production of a number of fertilizer materials. By the addition of a hydrating plant quite similar to the one at present installed, lime nitrogen as it comes from the mill room could be oiled and hydrated so as to render it usable as a fertilizer. This additional plant would cost about $250,000 and would have an annual capacity of 220,000 tons of material. The new equipment would consist principally of a cut flight conveyor fitted with water and oil sprays. A building for storing this product would also be required.

The present final product for which the nitrate plant is designed is grained ammonium nitrate. This material is too liable to cake and too deliquescent to be very satisfactory in mixed fertilizers. However, by the expenditure of a few thousand dollars for oil containers this product can be coated in the present grainers, rendering it suitable for use as a fertilizing material.

The material which must perhaps be the main output of the plant at first is ammonium sulphate. This is a standard material and can be readily absorbed in mixed fertilizers and used to some extent as a top dressing. To produce this at the Muscle Shoals plant, it would be necessary to erect a neutralizer plant consisting of saturators in which ammonia gas from the autoclave building is passed through weak sulphuric acid, drain tables for the building up of crystals.

centrifuges for wringing out the greater part of the liquor, and dryers for drying the material to 1 to 2 per cent moisture. A building for storing, bagging, and shipping the finished product would also be required. Sulphuric acid can either be purchased outside and stored in a storage plant, which would have to be erected, or produced at the site by the contact sulphuric acid units now in storage there.

One of the most attractive possibilities is that of producing ammonium phosphate, which, with cheap phosphoric acid, would be the ideal material. The same plant used for the production of ammonium sulphate can be used for ammonium phosphate. Phosphoric acid for this product would have to be that as produced in the electric furnace to be cheap enough to permit ammonium phosphate to compete with other fertilizers. This would require the erection of an electric furnace phosphoric-acid plant.

Another possibility is that of mixed salts. The double salt of ammonium nitrate and ammonium sulphate, which is being manufactured on a considerable scale in Germany, although not as concentrated a fertilizer as ammonium nitrate, is a relatively concentrated fertilizer substance and is considerably less hygroscopic than ammonium nitrate. Besides a plant for the production of ammonium sulphate, there would be required a series of mixing tanks, evaporating pans, and centrifuges. The cost of this material per ton of contained nitrogen, however, would be less than for grained and oiled ammonium nitrate. The mixed salt of nitrogen and potash is a nondeliquescent salt possibility, produced by the double decomposition of ammonium nitrate with potassium sulphate or with potassium chloride. These materials could be manufactured in the same equipment suggested for the production of the double salt of ammonium sulphate and ammonium nitrate. They are highly concentrated fertilizers, containing both nitrogen and potash and are of excellent physical quality, provided potash of good grade is used.

Urea, a material at present produced in Germany for export to America, while too costly of production at present to be used as a fertilizer, is used in the manufacture of celluloid and could quite readily be produced at United States Nitrate Plant No. 2.

Besides these there are other possibilities, chief among which are dicyanodiamide and nitroguanidine.

It was, therefore, decided that the only way to secure that the nitrate plants shall be always immediately available for most efficient military service, and for most efficient and economical extension in case of need, is to operate them continuously, whether in peace or war. As the river power plant had capacity to operate the plant at 80 per cent capacity, or eight carbide furnaces, and inasmuch as power brought from the Warrior station was unduly expensive, operation of the nitrate plant until the advent of cheap hydroelectric power from the Wilson Dam was recommended by the fixed nitrogen administrator at 80 per cent capacity as follows: Four furnaces (or 40 per cent of plant capacity) for the manufacture of 86,000 tons of ammonium sulphate per year; one furnace (or 10 per cent of plant capacity) for the yearly manufacture of 22,225 tons of dry cyanamide, making 24,445 tons of hydrated and oiled cyanamide; two furnaces (or 20 per cent of plant capacity) for the manufacture of 22,000 tons of ammonium nitrate; one furnace (or 10 per cent of plant capacity) for the manufacture of cyanamide, ammonium sulphate, ammonium nitrate, or intermediate product according to demand.

To accomplish this it would be necessary to erect and equip a plant for oiling and hydrating 200 tons per day of cyanamide, for producing 300 tons per day of ammonium sulphate, storage and bagging facilities for all products; acid storage of 20,000 tons capacity, purchase tank cars, shipping containers, sidings, etc., at the total estimated cost of $3,000,000.

In addition there would be required a working capital for raw materials, supplies, etc., of $6,600,000 and a general-purpose fund of $2,500,000, or a grand total required of $12,100,000.

It was further recommended that these operations should be carried out by a corporation which should be formed to take over all of the fixed-nitrogen assets of the War Department, and to perform all of the duties of administering these plants and funds in peace time, while continually enhancing their military value.

To this end there was introduced to the Senate on November 3, 1919, by Senator Wadsworth a bill, S. 3390, entitled "An act to provide further for the national defense; to establish a self-sustaining Federal agency for the manufacture, production, and development of the products of atmospheric nitrogen for military, experimental, and other purposes; to provide research laboratories and experimental plants for the development of fixed-nitrogen production; and for other purposes"; and a similar bill, H. R. 10329, to the House of Representatives on November 1, 1919, by Representative Kahn.

These bills were referred to the Senate Committee on Agriculture and Forestry and the House Committee on Military Affairs, respectively.

Extensive hearings were held by the Senate committee between March 22 and April 28, 1920, and in June this committee recommended the bill favorably to the Senate in session. Congress adjourned, however, the end of June before a vote had been taken.

During the first part of January, 1921, the third session of the Sixty-sixth Congress, this bill, S. 3390, came up for debate of the

Senate in session, and on January 13, 1921, the bill quite materially amended was passed by the Senate and sent to the House of Representatives, which body on January 15 referred it to the Committee on Military Affairs.

The Sixty-sixth Congress adjourned sine die on March 4, 1921, with the bill never having been reported out of the committee.

In the meanwhile hearings on H. R. 10329 were held by the Military Affairs Committee on April 19, 1920, but this bill was never reported out and, like its sister bill S. 3390, "died in committee."

A test on these bills was made in Congress during the latter part of February, 1921, in connection with a Senate amendment to the sundry civil appropriation bill, which would appropriate $10,000,000 for the continuation of construction of the Wilson Dam which would make available cheap hydroelectric power for the operation of the nitrate plant. This amendment, however, was removed in conference.

By this time complete process and construction designs and details of a plant for the manufacture of 86,500 tons per year of ammonium sulphate had been made, as had also plans and designs for facilities for storing 20,000 tons of 60° Baumé sulphuric acid; for the oiling and hydrating of calcium cyanamide; and for the erection of the four contact sulphuric acid units of a combined capacity of 240 tons of 100 per cent sulphuric acid per day which had been dismantled at the Old Hickory powder plant, near Nashville, Tenn., and placed in storage at United States Nitrate Plant No. 2.

In working up a design for the sulphate of ammonia plant the fact was kept in mind that it might later be desirable to manufacture phosphate of ammonia as well. Accordingly the equipment was so designed as to be, with very small change, utilizable for the production of ammonium phosphate, and, further, this equipment was arranged into four units, each capable of independent operation, and also so arranged that ammonium sulphate and phosphate could be produced at the same time. The estimated cost of this project, together with sulphate storage, bagging, and shipping, was $1,350,000.

The Warrior station, in accordance with privileges granted the Alabama Power Co. in the original contract, is now being operated by that company for its own purposes at a return to the Government of 1½ mills per net kilowatt hour of energy produced by the contractor at the Warrior extension and measured at the Warrior extension switchboard.

The United States Nitrate Plant No. 2 is now, with the exception of the Warrior station and the plant auxiliaries, such as the water and sewerage systems and equipment necessary for proper maintenance, being maintained in idle stand-by under periodic inspection by a mechanical engineer in private practice, and is, therefore, available for practically immediate emergency use.

a. Wilson Dam.—Carried with the thought of nitrate plants there was ever present the thought of cheap hydroelectric power, and this thought was more or less concentrated on the Tennessee River.

Surveys and studies of the Muscle Shoals section of the Tennessee River had been made and reported as early as 1828. These reports, however, were looking toward the rendering of the river navigable by means of canals. But in 1907 the Corps of Engineers rendered its first report on the development of this water power by means of dams. This and the several subsequent reports dealt with the combined power development and navigation improvement.

In its report of January 20, 1917, the committee of scientists and engineers selected by the president of the National Academy of Sciences at the request of the Secretary of War recommended that the Government should provide for the development of processes for the fixation of atmospheric nitrogen on as large a scale as possible by developing at a suitable location as much hydroelectric power as possible with the appropriation available.

This referred to the $20,000,000 appropriated by the President under "section 124, nitrate supply," of the national defense act.

Accordingly, on November 16, 1917, an allotment of $500,000 was made the Chief of Engineers for the acquisition of necessary lands and for the beginning of construction of Lock and Dam No. 2 at Muscle Shoals, and on February 23, 1918, an additional allotment of $12,630,000 was made for the completion of this lock and dam.

However, due to the extreme stringency of the labor and material and supply markets, and in consideration of the fact that in all probability power from this source would not be available for the then present emergency, the estimated time of completion being from four to five years, actual construction was deferred early in the spring of 1918 until more opportune conditions should prevail.

Almost immediately upon the signing of the armistice, therefore, work was resumed on a large scale.

The dam, which is to be nearly a mile in length, will create a head varying from about 70 feet at extreme high stages of the river to about 100 feet at extreme low stages, with a normal head of 95 feet throughout the greater portion of the year.

Four generating units, each of 20,000 kilowatts, driven by four 30,000-horsepower hydraulic turbines, are under construction. The installation of additional power units, up to a total of about 500,000 horsepower, is under consideration. From a careful study of the flow of the stream over an extended period of time, it is estimated that of this power generated there will be 87,300 primary horsepower, with 53,700 secondary horsepower, available for 10 months of the year, an additional 165,500 horsepower available for 6 months, and the remainder for shorter periods dependent upon river conditions.

By early 1921 quite material progress had been made, and of the $17,000,000 available nearly $12,000,000 had been expended, necessitating, therefore, an additional appropriation for continuance of construction.

To care for this there was placed into the sundry civil appropriation bill, 1922, Senate amendment No. 60: "Nitrate plants.—For continuing construction of locks, dams, power house, and appurtenances authorized by the national defense act, approved June 3, 1916, $10,000,000."

This amendment was, however, removed in conference, and Congress adjourned without any provision being made for continuing the construction of the Wilson Dam.

By May, 1921, with the project approximately 35 per cent complete, practically all progress had been discontinued.

On the north shore there were the main offices, the housing for the military and technical and executive civilian employees, and quarters for about half of the labor force. This end of the dam showed such progress as to permit of the removal of the cofferdam; in fact, some sections here had reached finished height. The southern end of the dam, while still below cofferdam, was nevertheless showing rapid progress.

The island midway between shores, and a part of which upon the completion of the dam will be submerged, was the site of the large crushing and mixing plant. The section of dam across this island had been poured to three-quarters its finished height.

This then left an open channel to accommodate the flow of the river on each side of the island.

There now remains at this project a small force of guards and caretakers.

3. United States Nitrate Plants Nos. 3 and 4.

The need for a greater supply of ammonium nitrate than had been provided by the projects of United States Nitrate Plant Nos. 1 and 2 became manifest during late 1917 and early 1918. The war program as developed showed demands for explosives greatly exceeding the supply which could be relied upon, even after the provisions made by the erection of the large plant at Muscle Shoals.

The successful operation of the German troops in France and the program for sending United States troops to the front made the demand for enormous supplies of explosives, while the success with which the German submarines were then operating and the shortage of cargo vessels available as sodium nitrate carriers from Chile made it manifest that the explosive nitrogen must be produced in our own country. The only source for this was additional atmospheric nitrogen fixation plants.

At a conference on February 4, 1918, between Assistant Secretary of War, the Acting Chief of Ordnance, the Second Assistant Secretary of War, and Messrs. Baruch, Somers, and McDowell, of the War Industries Board, it was decided that the situation should be met by immediately starting on the erection of a plant for the fixation of atmospheric nitrogen and production of ammonium nitrate of a yearly capacity equal to the plant 2 project, or 110,000 tons ammonium nitrate, this project to be carried out by the Nitrate Division.

This decision was approved by the Secretary of War on February 5, 1918.

A survey of the process studies being conducted was made, and the search for sites renewed.

Meanwhile the Assistant Secretary of War, under date of March 26, 1918, appointed the following to constitute a "nitrate committee," later changed to "nitrate commission": Dr. Arthur A. Noyes, chairman; Brig. Gen. Chas. B. Wheeler, Rear Admiral Ralph Earle, Dr. Chas. L. Parsons, Mr. Leland L. Summers, Mr. Gano Dunn, Dr. Willis R. Whitney.

This commission was introduced to "advise in regard to the construction of an additional plant for the production of nitric acid or ammonia."

By invitation of the commission, its sessions were attended by Col. J. W. Joyes, Chief of Nitrate Division; Col. Odus C. Horney, representing the Surveyor General of Supplies; and by Messrs. Walter Robbins and Frederick Darlington, representing the priority and power committees of the War Industries Board.

At this time, the latter part of March, 1918, the Germans had broken through the line at St. Quentin, emphasizing the need of haste. The small and rather experimental plant, United States Nitrate Plant No. 1, employing the General Chemical Co.'s modified Haber process was not far enough advanced and would not be for four or five months to demonstrate that it would work.

Accordingly, the commission sat immediately for the specific purpose of considering the emergency, and on March 30, 1918, presented a report in part, as follows:

> *Resolved*, That in view of the urgency for immediate decision the committee confine itself in the selection of processes to a choice between the General Chemical Co.'s process and the American Cyanamid Co.'s process.
>
> *Resolved*, That in view of the present emergency and the necessity for obtaining ammonia, the cost being secondary in the present emergency, the committee recommends that the new nitrate project, known as project No. 3, be constructed and operated under the cyanamide process.

Pursuant to this recommendation, and urged to prompt action by the Secretary of War and by the chairman of the War Industries Board, negotiations were intiated with the American Cyanamid Co. looking to the construction of additional plant or plants of the aggregate capacity of the Muscle Shoals plant, 110,000 tons of ammonium nitrate per annum. By common consent this new agreement was to supersede that of November 16, 1917, and cover the construction and operation of not only the additional project No. 3, but also the original plant at Muscle Shoals.

Negotiations were carried along for nearly two months under great pressure, difficulty, and stress, and at a serious loss of valuable time. Progress was very slow. Finally, on June 8, 1918, after the Air Nitrates Corporation had been advised that a conclusion must be reached by 6 o'clock in the evening of June 8, the points of disagreement were finally settled and an agreement signed.

This contract followed the contract of November 16, 1917, closely in many of its provisions, which seemed the only basis on which an agreement could be reached, but contained a clause to the effect that the agent should from time to time consult with the contracting officer upon the general character of the work contemplated, which was intended to afford the United States the authority for exercising such control and direction of the operations of the Air Nitrates Corporation under the contract as the developments of the situation might necessitate. The contract also fixed the maximum fee to the contractor at $1,500,000.

While these negotiations were taking place the search for a site revealed Kingsport, Tenn., as being the most opportune from the viewpoint of construction and supply of the necessary raw materials. This site was therefore recommended, but was objected to by the electrical committee of the War Industries Board on the ground that as the necessary power was not available in that vicinity it would be necessary to erect a 90,000-kilowatt generating station, the generator for which they would be unable to supply. It then developed that the Tennessee Power Co. had available enough power for half the plant, and it was recommended that plant No. 3 be built in two identical units, each of a capacity equal to one-half the Muscle Shoals plant, with unit 3–A situated at Kingsport and 3–B at Clinton, Tenn. Unit 3–B was to receive its power supply from the line of the Tennessee Power Co.

This selection was not entirely satisfactory, however, and a further study of the power situation disclosed available power in Ohio and a site for 3–A, now known as United States Nitrate Plant No. 3, was selected and approved just outside of the city of Toledo, and 3–B, known as United States Nitrate Plant No. 4, at Broadwell, Cincinnati.

The condition which had developed in connection with the construction work on No. 2 plant indicated clearly the importance of having the interests of the United States safeguarded through a competent and responsible representative thoroughly experienced in construction undertakings of an intricate character and on a large scale. Mr. Frederick L. Cranford after a study of the situation consented to undertake the supervision of the work involved in the completion of No. 2 plant and the construction of plants Nos. 3 and 4. Mr. Cranford, although not formally appointed director of construction until July, assumed his duties in June.

The conditions pointed clearly to the importance of avoiding at plants Nos. 3 and 4 the mistakes of Plant No. 2, and a set-up was arranged by Mr. Cranford calling for a single responsible organization at each plant, avoiding duplication of effort and divided responsibility.

Under date of July 31, 1918, a joint recommendation signed by Brig. Gen. R. C. Marshall, jr., in charge of the Construction Division of the Army, and Colonel Joyes, Chief of Nitrate Division, to the effect that in the completion of United States Nitrate Plant No. 2 and in the construction of plants Nos. 3 and 4 the Construction Division of the War Department act for the Nitrate Division in matters relating to construction, was approved by the Assistant Secretary of War.

Accordingly, the construction quartermaster arrived on the premises at Toledo on August 12, 1918, and immediately assumed charge of the construction of United States Nitrate Plant No. 3.

The site for this plant embraced approximately 650 acres of the so-called Autokee, Navarre, and Wasajaw tracts, a flat peninsula-like property surrounded by the Maumee River and Duck and Otter Creeks.

The president and chief engineer of the Bates & Rogers Construction Co., of Chicago, retained as general contractors, arrived at the site July 29 and laid out plans for carrying out the work, which started almost immediately.

The first construction materials to arrive, lumber and nails, were received August 8, and from then on an average of 37 cars per day were received and unloaded.

This plant was to be similar in every respect except size to the No. 2 plant at Muscle Shoals. Because of its nearness to Toledo, however, it was not necessary to provide for an industrial village, and only about half of the construction force had to be housed, thus allowing of almost full attention from the outset to the permanent manufacturing plant.

The power for the plant was to be supplied by the Toledo Rail & Light Co. of Toledo to the extent of 40,000 horsepower and to be transmitted from their generating station located within the city of Toledo, a distance of 4 miles, over a standard, steel-tower, high-tension transmission line.

The Chemical Construction Co. was engaged under date of October 30 1918, as in the case of plant No. 2, to design, erect, and construct the nitric acid recovery and neutralizing plants.

The construction superintendent under this contract arrived September 4, and by October 9 the work of acid-proofing the foundations was started, and the first masonry work October 14. The first construction materials for this work arrived September 20.

Although handicapped somewhat by exceptionally rainy weather, excellent progress was made on the whole plant, and by the time of the signing of the armistice, November 11, practically all foundations for the permanent buildings had been completed, 80 per cent of the equipment foundations and the superstructure of the carbide mill, lime nitrogen oven, lime nitrogen mill, machine and engine shop, blacksmith shop, woodworking shop, autoclave and filter building and process steam plant either completed or practically so.

The site of United States Nitrate Plant No. 4, later called Ancor, Ohio, is in the valley of the Little Miami River, some 10 miles above its junction with the Ohio River and 13 miles northeast of Cincinnati. It lies on the east bank of the river and extends eastward to the hills about 5½ miles.

This plant, with a capacity of 55,000 tons of ammonium nitrate per year, was to be an exact duplicate of plant No. 3 at Toledo.

Contract for the general construction was awarded, under date of July 26, 1918, to the George A. Fuller Co., of New York, and, as in the case of plants Nos. 2 and 3, the construction of the nitric acid recovery and neutralizing plants was placed with the Chemical Construction Co. This contract was dated July 27, 1918.

The labor requirements for the construction of this plant were estimated at 10,000 employees, and owing to the distance from the labor market it was deemed necessary to provide housing facilities for at least half of these. Great difficulty was experienced, however, in recruiting the necessary labor, and by October 23, 1918, the labor peak of 5,183 was reached.

Construction of this plant may be said to have begun on July 6, 1918, when the work of running land lines and taking topography was started.

On August 8, 1918, construction of a pontoon bridge across the Little Miami was started to connect the plant site with the C. M. & L. Interurban traction line. On August 15, 1918, the first labor train on the Pennsylvania Railroad was run from Cincinnati to the plant site. Between this date and December 28, 1918, a total of 352,991 workmen had been transported.

On August 18, 1918, the constructing quartermaster reported and immediately assumed his duties. The first work on the manufacturing plant started on August 28, with the excavation for the absorption building. On September 6 the pouring of the footings for this building was started.

A campaign for labor was inaugurated on October 3, 1918, and vigorously prosecuted by the constructing quartermaster, with the aid of Mayor Galvin, of Cincinnati; Judge Lenders, of the probate court of Hamilton County; and others. This campaign showed good results, but by October 9, 1918, the total employees were only about 50 per cent of requirements.

At the time of the signing of the armistice foundations for all the permanent buildings were well underway and nearing completion, while structural steel for the autoclave and filter building and for the absorption building was all erected and bolted in place. The machine shop, blacksmith shop, and woodworking shop were entirely complete, with the exception of the installation of the electrical equipment. The whole project at this date was 18 per cent completed.

Upon the signing of the armistice all construction on these projects was discontinued, and the memorandum from the Assistant Secretary of War—Director of Munitions—dated December 2, 1918, and which directed that plant No. 2 be completed and operated sufficiently to demonstrate its capacity and efficiency, also directed that plants Nos. 3 and 4 were not to be completed as ammonium nitrate plants; that certain smaller buildings on which considerable work had already been done were to be completed for storage purposes. Work on all outstanding subcontracts for building materials, machinery, and equipment was ordered discontinued, and negotiations for the adjustment of all claims arising from the suspension of such contracts were entered into.

The total gross expenditure for plant No. 3 was $7,193,670.30, while the gross cost of plant No. 4 was $7,321,373.17.

These plants were eventually transferred to the Ordnance Department Salvage Board, and the materials, with the exception of a few buildings retained for storage purposes, disposed of.

The early summer of 1918 found the probable supply of nitrates still behind the demands as estimated for the year 1920, and on August 2 and again on August 15 the Assistant Secretary of War requested the nitrate commission to consider additional sources of supply.

Accordingly this commission rendered a report under date of August 24, 1918, recommending, among other things, that the Nitrate Division actively supervise and assist in the development of the cyanide processes of the Air Reduction Co. and the Nitrogen Products Co.; that there be established in the vicinity of Washington a nitrate experiment station under the control of the Nitrate Division, in which laboratory experiments could be made and processes for the manufacture of nitrogen products be tested and developed on a semi-industrial scale; that the construction of new fixation plants of a total capacity equal to that of the combined capacity of plants Nos. 2, 3, and 4, as recommended and urged by the chairman of the War Industries Board, be held in abeyance pending results of the synthetic process of the General Chemical Co. and the British Government, the cyanide processes of the Nitrogen Products Co. and of the Air Reduction Co., and the nitride process of the Aluminum Co. of America.

Under date of September 3, 1918, these recommendations were approved by the Acting Secretary of War.

Events in Europe soon indicated, however, that the construction of further fixation plants would be unnecessary, and even before the signing of the armistice the project had been abandoned.

4. United States Chemical Plant No. 4. Saltville. Va.

In his report of January 27, 1917, previously mentioned, the chief chemist of the Bureau of Mines made mention of the cyanide process for fixing nitrogen. He reported that, while that process was not yet a commercial success, it had great possibilities. He again adverted to this process in his report of April 30, 1917, mentioning a proposal as made by the Nitrogen Products Co. for the use of their cyanide process by the Government, and recommended that $200,000 be set aside for active experimentation on a large scale on the cyanide process, this experimentation to be conducted at Saltville, Va., at the site of the then present plant of the Nitrogen Products Co., where nitrogen, soda, and coal were available.

During the summer of 1917 reports from the French and English field laboratories showed the desirability of cyanide compounds incident to gas warfare, and in October the French High Commission appealed to the United States for aid. As a result of the study following this appeal the Secretary of War, on November 26, 1917, accepted a proposition of the Secretary of the Interior and authorized him to proceed with the erection of a plant to produce 10 tons per day of sodium cyanide by the Bucher process.

An appropriation of $750,000 was made available on December 27, 1917, and the design was started on January 2, 1918, in Washington, under the immediate direction of the chief chemist of the Bureau of Mines, for the trench warfare section of the Ordnance Department.

The rights to the use of the Nitrogen Products Co.'s Bucher process had been obtained, although the contract between the Chief of Ordnance and this company was dated as late as February 28, 1918.

The site, Saltville, Va., besides having been recommended by Doctor Parsons, was urged and demanded by the Nitrogen Products Co., first, because of the waste nitrogen which they agreed to furnish free, and, second, because that company refused to allow the Government to use their process, except by commandeering, at any other site; thus insuring that it would not be erected near a competitive process. Although other sources of nitrogen were available elsewhere, it was not the policy of the Chief of Ordnance to commandeer, and this place was selected.

The supply of free waste nitrogen, however, did not materialize, and it was necessary for the Government to install nitrogen columns of the Claude process. The selection of this site further proved to be unfortunate because of the local railroad facilities and the general inaccessibility of the locality to the machinery producing and other markets.

Saltville is in Smythe County, Va., in the heart of the mountains of southwest Virginia, 1,700 feet above sea level. The town, which has a population of 2,000, is owned and controlled entirely by the Mathieson Alkali Works, parent organization of the Nitrogen Products Co. As there were no quarters available for Government employees in this town, Doctor Wilder, of the Southern Gypsum Co., 4 miles distant, in a spirit of cooperation, provided quarters for some of the force at the Gypco Inn until Government quarters at the site were available.

The construction of this plant was placed with the Construction Division of the Army, which division, under date of February 25, 1918, entered into contract with Fraser, Brace & Co., of New York, for the general construction and installation of plant and equipment.

The constructing quartermaster assigned to this job on February 3 visited the site, the following day returning to Washington to aid in the design and expediting of construction materials and plant equipment. He took up his station at Saltville on March 11.

Construction started on March 6, and on March 19 the spur track to the site had been placed and ready for use. A second spur was completed on March 22, and materials at the rate of 5 cars per day, increasing to 26 per day, were received.

The first structures to be erected were barracks for use as quarters for the contractor's force. This was followed by grading the manufacturing site, which, because of the heavy rains, showed slow progress and was not completed until May 9.

Although labor was extremely scarce, it entered into the spirit of nesessary speed, and the ball mills and dry mixers in the mechanical preparation building were turned over to the commanding officer and were put into operation on September 10. The first nitrogen column was completed and started operation on September 13, at which time the balloon and booster pumps were completed. The gas producers were placed in operation on September 16, followed by six banks of furnaces on the 20th, thus completing a cycle. The various utilities—steam, electrical, water, and sewerage systems—were far enough along to permit of this small-scale operation and were turned over to the commanding officer as completed. By November 2 the plant had been wholly completed and an over-all transfer made.

During the process of construction a training school was conducted at the then operating plant of the Nitrogen Products Co. at Saltville, Va., to train operators. This training course started May 1, 1918, and continued until September 7, during which time 14 men had taken the full course in all departments and 12 others short courses of some particular process.

On September 4 wood fires were built in the ends of the gas producer crossheads and kept going until September 16, on which day, at 2.30 p. m., two gas producers were started up. By 8 p. m. these were producing good gas. On the 18th the first block of furnaces was gas fired. On the 19th cracks began to develop in the red brick shell of the furnaces; and although the tie-rods were tightened from time to time, examination after these furnaces were permanently shut down on January 5, 1919, showed that they had sagged and cracked and in some cases baffle walls badly sagged and the cast-iron pyrometer thimbles badly corroded.

Briquets were first put into one retort of block No. 8 on October 18. After a day's steady feeding only a fraction of a per cent of cyanide was obtained.

However, continued operation produced better results, until the week ending November 23 showed a production of 235 pounds of sodium cyanide, while the week of December 1 to 7, inclusive, yielded a total of 2,714 pounds. This was the largest weekly production during operation of the plant.

The first briquets ready for lixiviation were received from the retort building on December 2, and analyzed a little over 5 per cent sodium cyanide. A total of 7,599.8 pounds of sodium cyanide was produced during the total period of operation.

The gross cost of this plant was $2,384,350.

Under date of November 26, 1918, the Secretary of Interior informed the Secretary of War that the chemical plant No. 4, Saltville, Va., had been completed and was ready for operation; that all of the equipment had been tried out and the plant could be brought to full operation quickly at any time; and that as the funds had been handled entirely by the War Department no formal transfer was necessary. This plant was then officially placed under control of the Nitrate Division under date of December 19, 1918.

On January 7, 1919, the Secretary of War directed that the Director of Chemical Warfare Service appoint a board to investigate the Saltville plant and make recommendations as to its future. This board, consisting of four officers of the Chemical Warfare Service, was appointed under date of January 16, 1919. The report of this board submitted the latter part of March recommended that as the operation of the plant as a governmental or private enterprise for the production of cyanide or of ammonia was not considered feasible for the reason that the operating costs were far in excess of the costs which could be attained by other processes already available, the plant be advertised for sale in whole or in part; and that if the bids received aggregate an amount of $1,000,000 or more the sale or sales be consummated, if not the plant be held until better business conditions prevail.

The Nitrate Division concurred in these recommendations, and although engineers for a number of large concerns investigated the proposition, no bids were received, and, effective July 10, 1919, the plant was transferred to the Cincinnati district ordnance office for disposition by salvage.

C. TECHNICAL RESEARCH.

At the time the Nitrate Division was organized in July, 1917, a research technical section was formed. This section carried on investigations at various points and in cooperation with many institutions and individuals, including other Government bureaus.

1. Laboratories of Nitrate Division.

a. Sheffield Experiment Station.—In the summer of 1917 it was recognized that the program of building and operating nitrogen fixation plants carried with it the corollary of establishing a laboratory wherein research might be made into the processes adopted in the plants. It had been originally intended to locate such a laboratory in the city of Washington, but as the funds available forbade this, a group of old buildings located on the plant No. 1 reservation was selected in October and remodeled to fit the purpose.

In general the investigations covered the catalytic oxidation of ammonia using platinum gauze with various types of oxidizing chambers; the absorption of nitrose gases; tests on acid-proof materials; the effect of nitric acid on aluminum; preparation of mixed acids; and others.

Experimentations continued here until January 15, 1919, when the station was closed. The personnel engaged on this work consisted of 23 commissioned officers, civilians, and enlisted men.

b. Arlington Farms.—For a matter of two or three years prior to the entry of the United States in the World War the Bureau of Soils had been interested in the synthesis of ammonia and had provided a testing plant at Arlington Farms, Va. In July of 1918 arrangements were made whereby the Nitrate Division took over this testing plant, with its personnel and facilities, in order to conduct tests on catalysts developed outside of the General Chemical Co.'s Laurel Hill laboratory.

In August the section became alarmed because of the difficulties which the General Chemical Co. seemed to experience in producing sufficient catalyst of a high grade for the requirements of the Sheffield plant. Accordingly a small catalyst manufacturing plant was installed, which started operations in October, 1918. On November 10 the plant was placed on a 24-hour, three-shift basis, and late in that month satisfactory conversions in testing catalysts were made.

Experiments were also conducted on efficient methods for supplying adequate quantities of hydrogen and nitrogen gases.

Operation continued here until April, 1919, when the plant was moved to the Fixed Nitrogen Research Laboratory.

In all this work great assistance was rendered by Dr. R. O. E. Davis, of the Bureau of Soils, and some of it carried on under his direct supervision.

c. Georgetown Experiment Station.—In August, 1917, Mr. James H. Reid brought to the attention of the Nitrate Division his process for producing calcium carbide and the fixation of nitrogen. Tests on his process were witnessed on several occasions at his laboratories at Sherman, Vt., and on July 3, 1918, his offer of June 27 to the President was accepted by the Secretary of War on behalf of the President.

This offer granted to the Government the use of his processes and designs of apparatus for the production of calcium carbide, for combining the same with nitrogen, and for obtaining from the same ammonia and therefrom ammonia compounds. For this Mr. Reid was to receive no compensation by the way of royalty or otherwise for the manufacture of products used exclusively in munitions of war, but was to receive a royalty of $5 per net ton of nitrogen produced for use in fertilizers, etc. He further offered his personal services in this connection at $1 per year.

An agreement was made with the Georgetown Gas Light Co., Georgetown, D. C., whereby a portion of their plant was turned over to the Nitrate Division to be used as an experimental station, and reconstruction and installation of equipment started immediately. However, at the time of the signing of the armistice this station was not ready for test, and further work was discontinued.

Under date of January 3, 1919, Mr. Reid withdrew his offer and asked to be discharged from all further responsibility.

d. Fixed Nitrogen Research Laboratory.—The report dated August 24, 1918, of the nitrate commission recommended as previously noted, that there be established in the vicinity of Washington a fixed nitrogen research laboratory, under the control of the Nitrate Division.

The Arlington Farms station was then being used by the Nitrate Division, but this, besides being the property of and required by the Bureau of Soils, was being used for testing catalysts for nitrate plant No. 1 and was inadequate for this new purpose.

Under date of June 1, 1917, the trustees of the American University, Washington, D. C., agreed to allow the Bureau of Mines to use their Ohio Building for experimental purposes.

Executive Order No. 61, dated June 27, 1918, transferred this building to the War Department for use under direction of the Chemical Warfare Service for the manufacture of toxic gases.

At the signing of the armistice the Chemical Warfare Service discontinued work on toxic gases at this station, and so had no further use for the Ohio Building and others erected by it. Accordingly, under date of March 29, 1919, the Secretary of War issued an order placing the Ohio Building, together with unutilized supplies, to the Fixed Nitrogen Research Laboratory of the Nitrate Division.

A discussion of the work and accomplishments of this laboratory is included in Chapter VI.

Effective July 1, 1921, the Fixed Nitrogen Research Laboratory was transferred from the control of the War Department to that of the Department of Agriculture.

2. Laboratories of Commercial Plants.

Extensive investigations into nitrogen fixation processes were made by the Nitrate Division in cooperation with various commercial companies, universities, and other institutions.

a. American Cyanamid Co.—At a conference held in Washington December 31, 1917, at which representatives of the Semet Solvay Co., General Chemical Co., American Cyanamid Co., Bureau of Mines, and the Nitrate Division were present, the field of ammonia oxidation was carefully canvassed and it was decided to install a multiple gauze nonelectrically heated converter at the plant of the American Cyanamid Co. at Warners, N. J. This type of converter did not work very satisfactorily on the cyanamide ammonia, efficiency of about only 80 per cent being obtained under the same conditions which had given 91 per cent on ammonia from coke-oven aqua. The trouble was apparently due to certain impurities which were present in minute amounts in cyanamide ammonia.

The results of these experiments indicated that the multiple gauze converter operating without heat would not operate successfully on cyanamide ammonia. The electrically heated flat gauze converter was therefore used at United States Nitrate Plan No. 2.

b. General Chemical Co.—The General Chemical Co. had at their Laurel Hill, Long Island, experimental station their experimental plant for the synthetic production of ammonia and was carrying on tests there on various phases of operation which would be encountered at United States Nitrate Plant No. 1, and on the testing of catalysts. An agreement was therefore reached whereby representatives of the Nitrate Division would be stationed at this station to study operation of the system, and later to assist in the manufacture and test of catalysts. The first of the Army representatives arrived at Laurel Hill October 27, 1917, and a study of the process started.

All operations of the process were tested on this laboratory plant and efforts then devoted to the production of catalysts, an order for which was placed by the Nitrate Division with the General Chemical Co. under date of January 19, 1918. No trouble was encountered in the manufacture of the CO catalyst. Preliminary work on the manufacture of ammonia catalyst was started April 16. The first lot, produced June 22, was very poor and only a small percentage was available for use. On June 25 the first lot was shipped to Sheffield. This was also poor catalyst, which led to the opening by the Government of Arlington Farms Laboratory. On October 12 work was started to double the capacity of the catalyst plant. This work was not completed at the time of the signing of the armistice, however, and construction was discontinued on December 13, 1918.

c. Nitrogen Products Co.—As the result of a tender submitted by the Nitrogen Products Co., the experiment station of this company at Greene, R. I., was operated under Government control between the dates of February 2, 1918, and December 2, 1918.

Investigations were made on the Nitrogen Products Co.'s cyanide process and tests made on charges as large as 600 pounds of briquets, showing that it is possible to recover from 85 to 95 per cent of the theoretical yield of ammonia from cyanized briquets without serious difficulty.

d. Air Reduction Co.—The Air Reduction Co. had developed a cyanide process at its plant at Jersey City, N. J., and first brought the attention of the Government to its process in July, 1917. Their plant was visited by the chief of the research technical section in August, 1917, when it was agreed that this company would carry on experimentation at its own expense. Reports of this work were so favorable that on August 5, 1918, a representative of the Nitrate Division was detailed to the Jersey City plant to make a further study of this process. He remained on duty there until November 18, 1918.

This process produced sodium cyanide through the interaction of nitrogen with sodium carbonate, iron, and carbon in a manner somewhat similar to that of the Bucher process.

e. Hercules Powder Co.—The Hercules Powder Co. had been experimenting on a sodium-cyanide process at their Kenvil, N. J., plant. This plant was visited in July, 1918, and a study of their process made; and although the Nitrate Division kept in close touch with this company, no developments of importance were noted. The feature of this process was operation at especially low temperatures and the use of an especially active charcoal.

f. General Electric Co.—A number of researches were initiated in the General Electric laboratory at Schenectady by Dr. Willis R. Whitney in cooperation with the Nitrate Division. These researches were chiefly on cyanide processes, and an electrically heated cyanide furnace of considerable dimensions was erected.

Doctor Whitney had been a member of the various nitrate commissions, and in October the research technical section succeeded in securing his services as director of research in an advisory capacity. Extremely valuable service was rendered by Doctor Whitney.

g. E. I. du Pont de Nemours Powder Co.—Through the courtesy of this company, Mr. F. J. Liljenroth was detailed to the Nitrate Division for several months in the summer and early autumn of 1918 to carry on a study of the arc process. The American Nitrogen Co., a subsidiary of the Du Pont Co., had done and were doing the chief work in this country on the arc process of nitrogen fixation.

Under Mr. Liljenroth's direction sketch plans for a plant to utilize 10,000 kilowatts in 3 Birkeland-Eyde furnaces and 15,000 kilowatts in 10 Schönherr furnaces were prepared. The scheme was to install and operate these furnaces in connection with the offpeak power from city systems, and so have a working basis in case conditions should render the construction of arc plants advisable. Provisional plans were also made for a plant to use 60,000 kilowatts on the Birkeland-Eyde system. At the signing of the armistice the work was discontinued.

h. Research Corporation.—An agreement was entered into with the Research Corporation whereby that company, as consulting engineers, carried on a cooperative investigation on the recovery of nitrous fumes and mists from nitrating plants through Cottrell precipitation. The work was done in the Research Corporation's laboratories.

3. Laboratories of Various Institutions.

a. Geophysical Laboratory.—Under date of May 14, 1918, Dr. A. A. Noyes, chairman of the Nitrate Research Committee, requested that the Geophysical Laboratory of the Carnegie Institute cooperate with the Nitrate Division on researches relating to the production of nitrogen compounds.

Dr. R. B. Sosman, acting director of the laboratory, was made responsible for the work, and under him the best microscopists, chemists, and physicists of the staff worked upon the problems.

The first work was on problems connected with the cyanide process. In July work was started on the General Chemical Co.'s process; first, a study of the Haber process catalyzers; then, in August, owing to the considerable variation in the results reported from the testing station at Laurel Hill, an intensive study of the General Chemical Co.'s catalyst was begun; and later, work to do with a carrier for the General Chemical Co.'s catalyst was taken up.

b. Bureau of Soils.—A very great service, as previously shown, was rendered by the Bureau of Soils in connection with the work carried on by the Nitrate Division at the Arlington Farms station and by the Fixed Nitrogen Research Laboratory. A study was also made on the electrolytic oxidation of ammonia in solution.

c. Bureau of Mines.—The cooperative work of the Bureau of Mines has been shown throughout this history. This bureau cooperated from the first with the Nitrate Division and, besides experimentation carried on in its own laboratories, rendered such service as has been shown in connection with the study of processes, selection of sites, and erection of the cyanide plant.

d. Bureau of Standards.—From July to November, 1918, the Bureau of Standards carried on research to develop a special apparatus for the determination of each of the gas constituents in the various gas mixtures throughout the synthetic-ammonia plant. This bureau also supervised the sampling and purifying of platinum to be used by the Nitrate Division as a catalytic material.

e. United States Geological Survey.—At the request of the Nitrate Division the Geological Survey carried on an exploration of domestic nitrate deposits to determine their value and possibility as a nitrogen source.

f. United States Assay Office, New York.—The platinum secured for use as a catalyzing medium at the nitrate plants was in the crude form. The assay office at New York undertook to refine this metal and draw it to coarse wire, and then gave very great assistance in concluding a contract for drawing and weaving this wire to the 0.003 diameter wire by 80-mesh gauze required.

g. Massachusetts Institute of Technology.—Laboratory experiments were made under the direction of Dr. A. A. Noyes at the laboratories of and using equipment of the Massachusetts Institute of Technology on the equilibrium involved in the formation of nitric acid from nitric oxide. It was determined that the reaction of NO_2 with water proceeded rapidly, while that of the oxidation of NO to NO_2 by air proceeded much more slowly. Various catalysts to accelerate this reaction were investigated, and it was found that certain forms of carbon such as were used in gas masks increased the velocity of reaction very greatly. As the process worked well on the laboratory scale, it was transferred to Sheffield, where on a larger scale serious trouble was encountered on account of the heat liberated in reaction and the work discontinued.

h. University of Michigan.—The University of Michigan cooperated with the Nitrate Division by studying, under Prof. E. D. Campbell, at the university's laboratory the purification of gases for ammonia synthesis.

i. Columbia University.—The chemical laboratory at Columbia University was made available to the Nitrate Division for experimental work in connection with the study on nitrous fumes being conducted by the Research Corporation.

j. University of West Virginia.—Prof. B. H. Hite, of the University of West Virginia, who was carrying on work looking to the production of hydrogen in pure form and at low cost from natural gas, reported on this work during the summer of 1918. In November plans were made for a thorough test of Professor Hite's method, and a thorough study made of the theoretical considerations.

k. Leland Stanford Junior University.—The services of Dr. E. C. Franklin, of the Leland Stanford Junior University, were secured in September, 1918, for work in connection principally with the various amides which might offer improvement over sodium amide for use in the United States Nitrate Plant No. 1.

Doctor Franklin had devoted a number of years to the study of ammonia compounds.

4. Other Investigations.

a. Nitride process.—The only nitride processes which attained promise were modifications of the Serpek process by the Aluminum Co. of America and the Armour Fertilizer Co. Both these companies kept the Government informed of their progress, and their plants were visited by the chief of the research technical section in the fall of 1918.

b. Henwood process.—This process, which was thoroughly investigated, involved the oxidation of ammonia by the use of free oxygen, the catalyst being a film of platinum on the surface of an alundun tube. No important results ever developed from this investigation.

c. Lunden process.—The Lunden process for the catalytic oxidation of ammonia in solution aroused much interest in the fall of 1918 because of the favorable opinion of it held by the British. Doctor

Noyes studied the little information obtainable upon the process when he was in England; and although negotiations for the purchase of the rights to the process by the Governments of the United States and Great Britain were started, further study revealed that the process was not as represented and the negotiations were abandoned.

D. UNITED STATES FIXED NITROGEN COMMISSION.

In December, 1918, at the request of the Assistant Secretary of War, Mr. Arthur Graham Glasgow, who in the summer of 1918 had, at the request of the Assistant Secretary of War, studied, in connection with his other duties in Europe, the nitrogen situation in the allied countries, visited Muscle Shoals with a view to making a study of the nitrate plants and recommending a plan for their future. Such recommendations were made in a memorandum dated January 7, 1919, and unanimously indorsed at the conference of January 14, 1919, between the Assistant Secretary of War, Chief of Ordnance, chairman of nitrate committee, Chief of Nitrate Division, Director of Construction, Mr. Glasgow, and others.

The Secretary of War, on March 29, 1919, after studying the recommedations which included the sending of a commission to Europe to study the plants in the various countries on that continent, including the occupied portions of Germany, appointed Mr. Glasgow his immediate representative in matters concerning the fixed-nitrogen interests of the War Department, with authority to act for him in all such matters—especially in connection with the administration of the Nitrate Division of the Ordnance Department, and the present and future disposition of the nitrate plants.

He further authorized that the Ordnance Department utilize for fixed-nitrogen research and development the abandoned "Ohio" laboratory of the Chemical Warfare Service at the American University, District of Columbia; that certain commissioned officers of the Army be retained in a civilian capacity to carry on this work; that active and progressive cooperation with the Navy, Interior, and Agriculture Departments and others be established in the task of endowing the Government's nitrate plants with maximum peacetime value for fertilization and other purposes.

In the Spring of 1919, therefore, Mr. Glasgow, the fixed-nitrogen administrator, informally appointed Col. J. W. Joyes, Ordnance Department, chairman; Lieut. Col. A. B. Lamb, Chemical Warfare Service; Lieut. Col. F. H. Wagner, Ordnance Department; and Capt. R. S. Tour, Ordnance Department, the United States Fixed Nitrogen Commission to visit and study the various atmospheric nitrogen-fixation plants of Europe.

Authority for the travel and confirmation of these appointments was given by the Secretary of War under date of May 28, 1919.

The commission sailed from Hoboken on June 6, 1919, and immediately upon arriving in France started on the tour of inspection. Great aid was given by both the French and English, and the German plants located in the occupied German territory were thoroughly inspected and studied during the time from July 3 to July 22 by the courtesy and aid of the French Control Commission.

The French plants visited included the temporary war plant at Nanteure, employing the cyanamide process and having a capacity of 30,000 tons of calcium cyanamide per year; that at Angouleme, for producing ammonia from cyanamide and having a capacity of 20,000 tons 100 per cent nitric acid per year; the nitric-acid plant at Toulouse; a private plant for producing cyanamide from charcoal at Marignac; a small calcium-carbide plant at Luclon; an arc plant at Le Pecq.

In Germany the large Haber-Bosch plants of the Badische Anilin und Soda Fabrik at Oppau and Merseburg proved of immense interest; and although the members of the commission were not allowed to make pencil notes much valuable information was obtained.[1] The Oppau plant had been in existence prior to the war, but had been enlarged to a capacity of 100,000 metric tons of nitrogen per year. The Merseburg plant was a war plant which started operation in 1917 and had a yearly capacity of 200,000 metric tons of nitrogen. The commission also visited the plant at Hoechst, near Frankfort, for oxidizing ammonia to nitric acid, and a similar plant at Leverkusen, near Cologne; and the German cyanamide and nitric-acid plant at Knapsack.

After returning to France the commission split, Colonel Wagner remaining in France, Colonel Lamb and Captain Tour proceeding to England, and Colonel Joyes to Norway to visit the celebrated large arc-process plants at Notodden and Rjukan.

Besides visiting these various plants, the commission met and conferred with many scientists of the allied nations, thus gaining much valuable information regarding both past experiences and future plans.

In Germany it was found that the cyanamide, Haber, and coke-oven plants were handled by a syndicate to regulate production, distribution, costs, etc.

The commission was intact again in the United States upon the return of Colonel Joyes on September 9, the other members having arrived a short time previous.

At this same time a number of agriculturists, among them Dr. Jacob G. Lipman, dean and director of the New Jersey State Agricultural Experiment Station, had visited Europe to study the nitrogen situation as regards fertilizing materials.

E. NAVY DEPARTMENT.

In the spring and summer of 1918 the Navy Department, in considering a source for future supply of explosive nitrogen, consulted with and studied the plans of the Nitrate Division of the Army Ordnance Department.

The result of this study was the decision to erect a plant for the fixation of atmospheric nitrogen according to the General Chemical Co.'s process, similar to United States Nitrate Plant No. 1.

The plant, which was to be erected at Indianhead, Md., was to have a rated capacity of 60,000 pounds of ammonia per day, and a daily production of 180,000 pounds of 96 per cent nitric acid by catalytic conversion and concentration.

Complete plans were ready and the contract let in September, 1918. While the process was to be that of the General Chemical Co., the contract for the construction and erection of the buildings and installation of equipment was awarded to the J. G. White Engineering Corporation.

The project, which was estimated to be completed in September, 1919, at a total cost of $9,000,000, was abandoned on November 5, 1918, the camp site only having been completed at that time.

F. UNITED STATES DEPARTMENT OF AGRICULTURE.

The activities of the Department of Agriculture regarding nitrogen research were confined to the Bureau of Soils.

In 1913 this bureau began its first investigation of the fixation of atmospheric nitrogen in studying the formation of nitrides. In 1916 investigations on four methods of nitrogen fixation, namely, the formation of nitrides, the cyanamide process, the arc process, and the Haber process, led the bureau to the conclusion that from the economic standpoint the method which held forth the most promise of success under American conditions was the Haber process.

During the summer of 1916 the department undertook to study the production of ammonia by the Haber process and began the installation of a small unit at Arlington Farms, Va., for this purpose. By August, 1917, an installation, modeled on the published accounts of the Haber process, had been completed. This was used for experimentation, and in January, 1918, the Nitrate Division assigned two men to assist on the work.

The plant was remodeled, and in September, 1918, was placed at the disposal of the Nitrate Division for testing catalysts in connection with United States Nitrate Plant No. 1, Sheffield, Ala. It was continued in operation at Arlington Farms until April, 1919, when it was moved to the Fixed Nitrogen Research Laboratory, on agreement to work in cooperation with the Bureau of Soils.

Independent study and work on the cyanamide and arc processes had been carried on previous to the establishment of the Fixed Nitrogen Research Laboratory, and since that establishment in connection with the laboratory.

G. UNITED STATES DEPARTMENT OF THE INTERIOR.

Besides the great aid rendered by the Interior Department, as mentioned throughout this chapter, the Bureau of Mines of this department had made, previous to the entrance of the United States into the World War, several studies of, and had conducted numerous experimental tests on, various subjects incident to the fixation of nitrogen. Early in 1917 the Bureau of Mines studied the catalytic oxidation of ammonia, using a single platinum gauze converter, and conducted tests at the plant of the Solvay Process Co., Syracuse, N. Y., using this type of converter. A type of converter similar to this was used at United States Nitrate Plant No. 2.

APPENDIX A.

UNITED STATES NITRATE PLANT NO. 1, SHEFFIELD, ALA.

The United States Nitrate Plant No. 1, designed to produce 22,000 tons of grained ammonium nitrate per year, is located on a site bordered on the northeast by the town of Sheffield, Colbert County, Ala., and on the northwest by the Tennessee River. The tract consists of 1,900 acres of rolling land, intersected by a creek supplying cold spring water in sufficient quantity for plant purposes. This plant stands on that portion of the site adjoining the town and covers an area of about 200 acres. Between the plant area and the creek is the industrial village for the housing of employees. The remainder and larger portion of the tract is covered principally by brush and timber and was purchased for the construction of an isolated experimental explosives plant, which was not built.

Water gas is manufactured for use in the production of synthetic ammonia, which in turn is oxidized to form nitric acid. The nitric acid can then be concentrated and disposed of as such or can, without concentration, be neutralized with ammonia to form ammonium nitrate in solution, later to be evaporated and grained. Auxiliary plant, including power house, pumping and filtration systems, machine shops, storehouse, repair and maintenance facilities of permanent construction were provided, while the chemical laboratory, hospital, and executive offices were of temporary construction.

The gas plant.—Water gas, which is the first material required in the operation of this plant, is produced in a standard water-gas plant of 4,000,000 cubic feet capacity per day, laid out in three separate units, each complete in itself and consisting of two gas sets, including generators, seals, wash boxes, scrubbers, blowers, and other auxiliary equipment so arranged that the sets may be operated either separately or simultaneously.

The generators are 7 feet 6 inch inside diameter by 13 feet 6 inches high, lined with Silcar brick and are fitted with rotary disk grates with drives. An auxiliary blast is placed around the machines 4 feet 5 inches above the grates. The take-off is brick lined and connected to the seal through 12-inch brick-lined fittings. The blast gases pass through a 15-inch stack valve into a steel stack. Coke is charged into the generators through the stack valve. Each generator has a standard 5 foot 6 inch diameter by 3 foot 3 inch seal through which the gas passes before it enters the 6 by 20 foot scrubber, which is filled with coke resting on trays and over which water sprays are directed. Pipe connections are such that gas from either generator may be passed through either or both scrubbers of each set. The gas is passed from the scrubbers into a three-lift 500,000 cubic foot capacity holder, from which it is passed through six iron-oxide purifiers placed on framework 13 feet above the ground. The purifiers are connected in pairs, so that either or both of any pair can be used with each generator set, and so that gas flow may be reversed through either purifier if desired.

Blast air pressure is obtained from two Sirocco blowers driven by 40-horsepower motors. The blowers are each so joined to the generators by a 12-inch line that either or both may be used with either or both generators. Air for the introduction of nitrogen into the gases is supplied by two 6 cubic foot Connersville blowers driven by two 30-horsepower motors. Steam is furnished from the power-house boilers and is measured by means of Bailey flow meters. Water service to the building is provided by a 4-inch main from the plant water system, which is supplemented by a supply from the Sheffield city water plant. Water consumption is measured by a 4-inch Worthington water meter. Coke dumped from cars into a track hopper is carried by an automatic skip hoist to a 100-ton elevated storage bin, from which it is delivered to the charging floor. A hydraulic elevator is provided as an auxiliary coke-handling apparatus.

The building in which the gas generators are housed is 44 by 136 feet, with an adjacent room 20 by 117 feet containing the blowers and other accessory equipment. The building is of steel frame with brick walls and limestone trim, concrete foundation, gypsum roof, and steel sash and doors.

The ammonia plant.—The ammonia plant is a direct synthetic process, constructed in accordance with the designs of the General Chemical Co., which company, after several years of experimentation, has somewhat modified the original German Haber process. The plant, built to synthesize ammonia at 100 atmospheres pressure, is divided into three separate units, Nos. 1 and 2, each having a rated capacity of 15,000 pounds of anhydrous ammonia per day, and No. 3, a capacity of 30,000 pounds per day.

In each unit a straight water gas or a mixture of water and producer gases is pumped from the gas plant by two Connersville blowers driven by 16-horsepower motors through a Venturi meter into three tubular heat interchangers and thence into a cast-iron catalyst chamber or converter 8 feet in diameter and 3 feet 8 inches deep. A mixture of producer gas and air, each constituent measured by a Venturi meter, is burned in an auxiliary heater built integrally with the main gas inlet of the converter, the purpose being to maintain the catalyst bed at proper reaction temperature and to supply necessary nitrogen from the burned air. The steam required for the chemical reaction in the converter, originally supplied through a steam superheater, is now to be furnished as low-pressure steam, being passed through a Venturi meter and into the gas main leading to the inlet of the second heat interchanger. Here the steam mixes with the main supply of gas and passes through two interchangers into the converter. The converted gas and excess steam, after chemical reaction, return through the three interchangers and are passed into steam condensers, from which the condensate is removed by means of a separator. The gases pass from the separator to a 25,000-

cubic foot holder, erected beside the main gas holder, for the purpose of maintaining a steady load on the compressors.

The gases are drawn from the small holder through a 6 by 28 foot buffer tank into two 4-stage (3–10–30–100 atmospheres) Nordberg compressors, which are driven by 300-horsepower motors equipped with Lenix drives. The gases from the compressors are passed through coolers equipped with separators into a water scrubber which is constructed of two 24½-inch by 13-foot cast-steel cylinders supported on cast-iron columns and with the ends closed by forged steelheads bolted to flanges which are screwed on to the ends of the cylinders. The scrubber is supplied with water by two 4 by 12 inch plunger type Watson Stillman Co. pumps, which are driven by 150-horsepower motors equipped with Lenix drives. The pressure of the water from the pumps is maintained steady by means of an accumulator floating on the line. The water from the scrubber passes to a Pelton water wheel direct connected to a 75-kilowatt generator which recovers the power of the discharging water. The flow of the water from the scrubber is regulated by a mechanical float mechanism which in turn controls a governor on the water-discharge nozzle. The water from the Pelton wheel discharges into the sewer. In case the Pelton wheel is not in operation, the water is by-passed from the float chamber directly into the sewer. The gases leaving the water scrubber pass through a separator for the removal of entrained moisture and enter the caustic scrubbing system.

The caustic system as originally installed consisted of a number of cylinders, pots, heaters, air lift, etc., and was intended for operation with hot caustic. In the process as modified to operate with cold caustic the gases pass into the lift together with the caustic solution and are lifted to the top of a single-cylinder scrubber similar in construction to the water scrubber. From here they pass to a receiver, which is a 60-inch diameter cast-steel pot, then through a coil and shell cooler, where the condensate and entrained caustic solution is removed and returned to the receiver, and through a catch pot to the next system. The catch pot prevents caustic solution from coming through with the gas and entering the next system. Two small pumps driven by 5-horsepower motors and with a small accumulator on the line are used to pump caustic solution through the system.

The gas is passed into a scrubbing system consisting of two single cylinders similar in construction to those of the previous systems, and through which a copper solution is circulated by means of three pumps driven by 5-horsepower motors and with accumulator on the line. The solution is introduced at the top of one cylinder, through which it passes downward and enters the top of a second cylinder, from which it is passed through a float chamber for level-control purposes into a regenerating system which consists of a 6-foot diameter by 6 foot 9 inch cast-iron tanks, glass lined, and fitted with steam coils. After regeneration the solution is passed through a brine cooler and returned to the scrubbers. The gases leaving the copper scrubbers are passed through a brine cooler from which condensed moisture is removed by means of separator and catch pot. They are then passed through driers and purifiers, which are 24½ and 36 inch diameter cylinders, respectively, filled with suitable drying and purifying materials.

Two small circulating compressors pump the proportioned gases from the purifiers through what is known as a circulating system, and which consists of an equalizer, heat interchangers, externally fired gas heater converter, and liquefiers. The equalizer is a 24½-inch diameter by 14-foot forged cylinder with a suitable packing through which the gases pass before they enter a series of three-heat interchangers. Each interchanger is made of a tube nest, each main tube having two others placed concentrically about it and the complete tube nest placed within a 24¼-inch diameter forged cylinder. The gases leave the heat interchangers and pass into a tubular heater fired externally and using producer gas as fuel. This heater brings the gas to, and maintains it at, the desired operating temperature. The gases leave the heater and pass into a 36-inch diameter by 15-foot converter, which contains a tube-nest filled with a catalytic material. Gases leave the converter, return through the three-heat interchangers, and pass into another interchanger, sometimes called cold interchanger, similar in construction to the others, and thence through two liquefiers placed in series. The liquefiers consist of a nest of coils placed within a shell, the gases passing through the coils and the refrigerant ammonia around them. The liquefied ammonia is removed by means of separators and catch pots. The refrigerant is furnished by standard refrigeration equipment consisting of 9 by 9 inch and 11 by 13 inch York compressors with their accessory condensors.

The ammonia taken from the catch pots is drained directly into 24-inch by 6-foot receivers placed outside of the building, from which it may either be charged into small cylinders for shipment or piped to other parts of the plant.

Vacuum pumps are installed to evacuate the system when commencing operation. Steam and compressed air are furnished by direct lines from the power house. Motive power is used at 220 volts direct current and lighting at 110 volts.

Unit No. 2 of the ammonia process is constructed substantially the same as unit No. 1, there being only a few changes in arrangement of equipment resulting from experience in the operation of unit No. 1. Unit No. 3 is similar in all its steps, but uses equipment of double the capacity of that in unit No. 1. In some instances the double capacity is obtained by the use of larger pieces of apparatus, while in other instances a double number of pieces of apparatus is used. Due to the signing of the armistice, however, units Nos. 2 and 3 were never completely installed.

The ammonia process building is 227 by 240 by 38 feet, and is constructed of steel framework, 12-inch brick walls trimmed with limestone, concrete foundations, and gypsum slab roofing. The building is divided into three bays, two of which are 75 feet wide and the third 90 feet wide for units 1, 2, and 3, respectively, and with two additional rooms containing switchboards and control apparatus.

Absorber house.—A small absorber plant to absorb ammonia gas not used in the acid plant, or to absorb anhydrous ammonia directly from the ammonia process, is located south of the oxidation building. The equipment consists of four complete units, each having five tanks for absorption. The ammonia enters the first three tanks of each unit in parallel and then passes through the other two in series. All but the last of these tanks are supplied with coils for water cooling. The aqua ammonia from the absorbers is discharged into a storage tank 16 by 45 feet. The building is one story with concrete substructure and asbestos-protected metal siding.

Ammonia oxidation and absorption.—The ammonia-oxidation or nitric-acid plant contains equipment for liquid-ammonia vaporization, aqua-ammonia vaporization, ammonia oxidation, and nitric-acid absorption. The liquid-ammonia vaporization consists of three sets of ammonia coils, one set on each floor and one floor above the other. The lower set of coils furnish chilled brine to a 60-ton ice plant and are inclosed in a cork room. The second set acts as a vaporizer and the upper set as a heater to bring the gas to specific temperature. A small centrifugal pump circulates warm water over the coils. The ammonia gas to be oxidized passes from the vaporizer to a gas holder, thence to a Thomas proportioning meter, where the ammonia is mixed with air. The mixture of ammonia and air is forced by a Buffalo fan into the mains leading to the converters. A Bailey fluid meter records the flow of ammonia from the vaporizer to the neutralizer. There are recording thermometers at the outlet of the vaporizing coils and at the outlet of the heater coils.

The aqua-ammonia vaporizer equipment consists of two 8 by 10 foot storage tanks, three Semet Solvay scrubbers, each with eight sections and with water-cooling chest on top and steam chest at the bottom, and one Connersville blower with a capacity of 12 cubic feet per revolution. The aqua ammonia through a regulating tank and measuring device is fed from the storage tanks to the scrubbers. One scrubber is equipped with a monte-jus for returning waste liquor to the storage tanks. A 1-inch liquid Venturi meter records the flow of aqua to each vaporizer, while Venturi meters record the air intake and air ammonia output of each vaporizer. Each vaporizer is equipped with recording pressure indicators and recording thermometers. All pipe is of cast iron.

The ammonia oxidation and nitric acid absorption part of the plant is divided into two units. The ammonia oxidation equipment consists of 14 converters of the cylindrical type, composed of a brick-lined sheet steel cylinder, into which fits the cylindrical form (9 inches diameter by 11.5 inches high) of a four-layer platinum gauze catalyst, held to the base and gas-inlet head by double ring clamps, and 1 activating converter of the flat gauze electrically heated type. A gas filter has been installed in the line just below the aluminum manifold. This filter and all piping to the converters is of aluminum. Each converter is equipped with a Bailey fluid meter and is supplied with auxiliary air and ammonia through 1-inch aluminum lines. A Uehling ammonia recorder keeps a check on the ammonia content of the ammonia-air mixture coming to the converters.ffiEach converter discharges its hot gases through an inverted U of 12-inch cast-iron pipe into a common collecting flue and from there into a cooler. The coolers are equipped with recording thermometers and pyrometers. Each nitric acid absorption system consists of a cooler, an oxidation chamber, and 2 blocks of 4 towers, each 34 by 34 by 60 feet. This cooling and absorption equipment is built in accordance with the designs of the Chemical Construction Co.

The nitrous oxide formed in the converter is absorbed by water in the absorbers and forms 50 per cent nitric acid. Each acid unit has a total capacity of 90,000 pounds of 50 per cent acid per day. The plant was equipped to vaporize either liquid or aqua ammonia so that the acid plant would be independent of ammonia supply from the direct synthetic plant and could utilize ammonia purchased from the coke oven or cyanamide industries. Two large tanks for storage of aqua ammonia are located between the ammonia process and ammonia oxidation buildings.

The oxidation and absorption building is of steel frame and asbestos-protected metal siding and roof. That part of the building which is used for absorption is 100 by 100 by 105 feet high, and that part of the building used for oxidation is 145 by 100 by 65 feet high.

A storage building 40 by 110 feet, of temporary wooden construction, covers three tanks of reinforced concrete and acid-proof masonry suitable for the storage of 1,800,000 pounds of weak nitric acid.

Acid concentration.—The nitric acid concentration plant concentrates from 50 per cent to 97 per cent at the rate of 24,000 pounds of 100 per cent acid per day per unit. The plant was designed for two such units, but equipment for only one was installed. Steam for this plant is obtained from the main line running from the power house. Weak acid is obtained through 3-inch duriron piping from the outside storage tanks. Concentrated sulphuric acid is piped directly from tank cars. Compressed air is furnished from the power house, and water is supplied by the plant system.

The concentrating system was designed by the Chemical Construction Co. The dilute nitric acid is carried by gravity through duriron pipe to an aluminum storage tank 12 feet 6 inches diameter by 10 feet deep, lined with acid-proof masonry and placed within the building. The acid is lifted overhead by 3-inch duriron air lifts to a similar tank from which it is discharged through a regulating device into a denitrating column, which is 42 feet high by 6 feet in diameter and lined with acid-proof masonry, packed with checkered brickwork, spiral rings, and quartz. The nitric acid vapor is taken from the top of the column to a condensing system, then through a Hough condenser used as a cooler, and discharged to the acid mixer or into an aluminum storage tank from which it may be passed outside the building to an acid mixer in which the strong nitric acid is mixed with sulphuric acid in preparation for shipment. The acid mixer consists of tanks 8 by 30 feet, in which paddles are actuated by means of motors. A set of water-cooled coils are provided for removing the heat due to the mixing of nitric and sulphuric acid. A 100-ton platform scale is used for weighing the acids. The remaining gas which was not condensed is passed into a set of acid-proof masonry absorption towers, in which the last trace of nitric acid is absorbed. The remaining gases are discharged to the atmosphere through duriron exhauster fan.

In connection with the nitric acid concentrating plant, there is a complete unit for the concentration of sulphuric acid. This unit consists of necessary steel tanks, lead-lined tanks, tower, blower, furnace, coolers, etc.

The concentration building is a steel-frame building consisting of a main part 85 by 125 feet by 65 feet high, and with a built-on wing

42 by 65 feet. The building is covered on sides and roof with asbestos-protected metal.

Ammonium nitrate plant.—The ammonium nitrate plant consists of a neutralizer building and two crystallizing buildings. The weak nitric acid from the oxidation building is carried to the neutralizer plant where it is mixed with vaporized ammonia brought from the vaporizers in the oxidation plant. Approximately 200,000 pounds of 56 per cent ammonium nitrate in solution may be produced per day from 30,000 pounds of ammonia vapor and 180,000 pounds of 50 per cent nitric acid. Acid from the storage tanks is lifted by a steam siphon to a 48,000-pound scale, where it is weighed and from which it is run by gravity into an aluminum supply tank inside the building. From the supply tank the acid is passed into the neutralizer, which is a large rectangular aluminum tank lined with acid-proof brick and covered by a brick arch, making the tank gas-tight. Vaporized ammonia is introduced through pipes placed at the bottom of the neutralizer. Excess ammonia, which is boiled off by the heat, due to the mixing, is passed through a condenser and into an absorption tower. The neutralized solution is run into two brick-lined steel tanks, from which it is pumped to the crystallizing building, approximately 1 mile away. The neutralizer building is 40 by 72 feet, covered with asbestos-protected metal, and is similar in construction to the acid plant.

There are two crystallization buildings located 500 feet apart as a safety measure in case of explosion. Each unit has a capacity of 75,000 pounds of finished ammonium nitrate per day. Ten-foot diameter by 16-foot storage tanks, with a capacity of 200,000 pounds of 50 per cent ammonium nitrate, receive the solution from the neutralizer building. The liquor is then run into rectangular glass-enameled steel evaporating pans 6 feet 6 inches wide, 11 feet long, and 30 inches deep. There are five of these pans per unit, and in each one there are placed 2½-inch aluminum coils carrying steam for evaporating purposes. Agitation of the solution is accompanied by means of a Connersville pressure blower driven by a 20-horsepower motor. Each pan has a hood over it to carry away evaporating liquid. Melted ammonium nitrate is drawn out of the pan through a special plug-valve and run into crystallizers, of which there are 10 for each unit. The crystallizers are the standard 5-foot jacketed type, geared to one line shaft driven by a 30-horsepower motor at each end. The ammonium nitrate is grained in these kettles and discharged on to a 14-inch conveyor, which discharges into a bucket elevator used for loading cars. Each building is 50 by 140 feet by 25 feet high, built on concrete foundations with steel framework and corrugated siding. Each building is separated by a fire wall into two parts, the evaporating room and the crystallizing room. There is also built at each end of each building a room in which the driving motors for the graining kettles are located.

Power house.—A 5,000-kilowatt (4,000 b. h. p.) power house furnishes all of the current and steam required for the operation of the plant and for the lighting of the village constructed in connection with the plant. The power house is 78 by 156 by 70 feet, on concrete foundations, with steel framework, brick walls with limestone trim, gypsum slab roof, and concrete floors. There are two 10-foot molded-block chimneys 200 feet high. The boiler room contains eight 500-horsepower Stirling boilers, equipped with Westinghouse stokers, superheaters, forced-draft systems, coal and ash handling equipment, including hoppers, crushers, elevators, conveyors, etc. The boilers are rated at 250 per cent maximum overload capacity and 200 per cent continuous overload capacity. The turbine room is equipped with two 1,875 and one 1,250 kv.-a., 190-volt alternating-current turbogenerators with equal synchronous rotary converter capacity, 40-horsepower motor generator sets, a 60-cell type "G" 19 Exide storage battery, 35-kilowatt exciter, 25-ton traveling crane, switchboards, and necessary auxiliary apparatus. A 250-volt direct current is used in the ammonia process and in the repair shops, but 2,300-volt alternating-current power is transmitted to other parts of the plant and transformed to 110 or 220 volt alternating current as required. On the basement floor of the power house there are two 100-pound air compressors, compressing air for process requirements, two 40-pound compressors for the air lifts in the oxidation plant, an air washer of 21,000 cubic feet per minute capacity, jet-type condensers, feed-water heaters, pumps, etc. Outside of the power house there is a 100 by 167 foot cooling pond with a capacity sufficient to cool 6,000 gallons of water per minute.

Just outside the power house a water-softener plant is located in a brick building 24 by 29 feet. The plant consists of pumps, mixing apparatus, regulating tanks, settling tanks, etc.

Auxiliaries.—A pumping station built in the shape of a decagon whose diameter would be 35 feet 9 inches was built at Spring Creek. The lower part of the building is constructed of reinforced concrete, while the upper part has a framework of steel faced with red brick. The mechanical and electrical equipment, consisting of three 2,500,000 gallon per day centrifugal pumps driven by induction motors, one Worthington No. 3 sump pump driven by induction motor, is located in the basement by the electrical switchboard, and apparatus that goes with this equipment is on the first floor, entrance to which is obtained by a concrete runway 90 feet long running from the hillside. A 20-inch water main leads to the filtration and storage system.

A booster pump house, 18 by 47 feet, of steel-frame and brick construction, is located near the acid plant and consists of four Chalmers centrifugal pumps driven by 20-horsepower motors. Three of these pumps supply the plant with 80 pounds of water, while the fourth supplies water to a 200,000-gallon storage emergency tank. A small booster station with four pumps in the pipe shop building supplies 40 pounds water to the gas plant and ammonia process.

The filtration plant, of 5,000,000 gallons per day capacity, consists of a sedimentation basin 100 by 60 feet, built of reinforced concrete, and on top of which was built the building to house mechanical equipment for filtration. The water for plant purposes is clarified and purified by dissemination, coagulation, and rapid sand filtration. Water for domestic use is further purified by chlorination.

A machine shop 60 by 112 feet by 35 feet high, steel framed, brick walls trimmed with limestone, 2-inch wooden roof covered with composition roofing, is equipped with a 10-ton bridge crane and with several medium-sized machine tools, such as lathes, drills, shaper, planer, grinder, saw, etc., required for ordinary repair work.

This shop does not contain tools heavy enough to handle the larger apparatus of the ammonia process.

The buildings known as the stores buildings were reconstructed from the main foundry building of the Sheffield Cast Iron Pipe & Foundry Co., and are now steel framed, covered with asbestos-protected siding. The main storeroom provides 30,000 square feet storage space inside, equipped with shelves, bins, scales, and 10-ton jib crane. In addition to 72,000 square feet used for a pipe and blacksmith shop and electrical repair shop, there is also 72,000 square feet of bulk storage space. This group of buildings houses the apparatus which makes copper scrubbing solution for the ammonia process and the apparatus used for the recovery of caustic-soda solution. There is also a small modern laundry built to serve the needs of officers, enlisted men, and of the hospital, and has a capacity estimated sufficient to care for 1,000 people. At the far end of this group of buildings there is maintained a garage with repair and storage facilities

A 22 by 36 foot one-story, steel-frame building with concrete foundation and metal siding was built near the concentration building for use as an oil storage house.

The main office was housed in a reconstructed wooden residence building. This office was only a temporary one, as was also the research laboratory, which was housed in an abandoned stove foundry building of wooden construction, and the hospital was also housed in a temporary wooden structure.

Direct current at 250 volts from the power house to the ammonia plant, machine shop, gas plant, and storehouse is carried in lead cables placed in vitrified tile ducts which are surrounded by concrete. Alternating current at 2,300 volts power is carried from the power house to the oxidation, concentration, and neutralization plants on overhead steel-pipe supports. Wooden supports carry the power to the pump house and to the village.

A complete telephone system of the common battery type serves the plant and village. All equipment except instruments are government-owned. The instruments are owned by the Southern Bell Telephone Co., with which the plant system connects.

A village was constructed about 1 mile southwest of the manufacturing area and consisted of 85 new stucco dwellings, 16 new frame dwellings, 9 remodeled frame dwellings, 2 frame dwellings not remodeled, 15 remodeled construction barracks, 10 construction barracks not remodeled, school building, 1 officers' barracks, in addition to a number of accessory buildings, such as heating plant, incinerator, etc. The village has all modern conveniences.

The plant and village are interconnected with the Sheffield city supplies of water and electricity. The plant is served by the Southern Railway system and there are about 4½ miles of sidetracks throughout the reservation. The village, which is about 1¾ miles from the town, is served by an interurban street railway system. Around the plant area there are about 19,000 feet of 20-foot roads with 6-inch slag base and 2-inch limestone surface. In the village there are about 5 miles of the same kind of road.

APPENDIX B.

UNITED STATES NITRATE PLANT NO. 2, MUSCLE SHOALS, ALA.

The United States Nitrate Plant No. 2 is located at Muscle Shoals, Colbert County, Ala., near the towns of Sheffield, Florence, and Tuscumbia. The Government reservation of 2,306.6 acres is contained in sections 13, 23, 24, 25, 26, and 27 of township 3 south, range 11 west, taken from the Huntsville meridian.

Beginning at the intersection of the low-water mark of the Tennessee River and the east section line of sections 13, 24, and 25, the property line runs south along this section line for a distance of 11,725 feet, thence west 11,500 feet, thence northeast and north along the eastern right of way of the Southern Railroad a distance of 8,530 feet to the low-water mark of the Tennessee River, and thence northeast along the river for 10,560 feet.

The center line or main axis of the manufacturing plant, which occupies a rectangular area 5,310 feet by 2,860 feet, runs north and south 3,400 feet west of the east property line.

The sequence of manufacture is, with one exception, from north to south this exception being the liquid air plant, which is located to the east of the plant using the nitrogen produced.

Limestone and coke, brought in over the west main line of the plant railroad system, are unloaded from a trestle at the north end of the manufacturing area, and from there either placed in raw-material storage or started into the process, as the conditions require. Coal for use at the river power house is also brought in over this line and unloaded from a trestle just north and west of the limestone and coke trestle, while coal for the limekilns is unloaded directly into the hopper at the coal mill building.

All materials from the unloading of the raw materials from the cars to the discharge of the finished ammonium nitrate from the grainers are mechanically handled by belt and screw conveyors, bucket elevators, electric traveling cranes, and pumps. There is installed in the manufacturing plant a total of 3,326 feet of 20-inch to 30-inch belt conveyor, 3,767 feet of 6-inch to 16-inch screw conveyor, and 1,846 feet of bucket elevators.

The description of the manufacturing plant will be taken up in groups according to the various processes involved.

Raw materials group.—The operations of this group consist of the preparation of the raw materials for use in the carbide group.

Limestone is burned in seven rotary kilns, 8 by 125 feet, which deposit the burned lime into seven rotary coolers, 5 by 50 feet, which serve the conveying equipment carrying the material to the raw material bins. This installation has a total rated capacity of 700 tons of calcined lime per 24 hours and is one of the three largest lime-burning plants in the world.

Fuel for the lime kilns is prepared in the coal mill building, which has a rated capacity of 336 tons of pulverized coal per 24 hours. The equipment consists principally of two Fuller 42 inches by 42 feet indirect-fired rotary dryers and four Fuller-Lehigh mills.

Coke is prepared in the coke dryer building by being fed through two crushing units, each of three sets of double crusher rolls to four 5 feet 6 inches by 40 feet rotary dryers, and from these dryers to the raw materials bins.

The raw material building consists of four 160-ton monolithic concrete silos for coke and four similar silos of 250 tons' capacity for lime.

Calcium carbide group.—The carbide furnace installation of 12 furnaces of 60 tons of calcium carbide capacity per 24 hours each constitutes the largest carbide furnace installation in the world. It is intended that but 10 furnaces should be operated at a time, leaving 2 for spares. Each furnace has three electrodes, 16 by 48 by 80 inches, which weigh, with the cooling head, 3,000 pounds.

The electrodes are prepared in the east end, for a distance of 100 feet, of the carbide furnace building, which is fitted up with four hand-fired ovens for baking the fire-clay coating to the electrodes, two planers, two 30-inch radial drills, and one wet grinder.

The carbide cooling building is a large shedlike structure in which the chill cars of molten carbide are placed. Upon cooling, this carbide is dropped to one of three inclined breaking platforms which serve the crushers.

The carbide mill building, in which are pulverized the broken carbide pigs, is equipped with three 30 by 42 inch Buchanan jaw crushers, three 10 feet diameter by 48 inches Hardinge ball mills, and three 7 feet diameter by 24 feet Smidth mills.

Cyanamide group.—The cyanamide oven building contains 1,536 ovens arranged in 16 rows of 96 each, resting on concrete slabs supported by concrete piers. A charge is loaded to these furnaces by means of the charging cars, of which there are four, each having four cylinders, thus permitting the charging of four ovens by each car at one time.

The maximum rated capacity of this plant is 750 tons of crude calcium cyanamide per 24 hours.

The ingots, which weigh about 2,000 pounds each, are removed from the ovens by means of an electric traveling crane and placed in the cyanamide cooling building where, after cooling, a tray of nine ingots is placed on one of the three concrete pedestals, from which one ingot at a time is let fall to the inclined breaking platform which serves the hopper of the crusher.

The cyanamide mill equipment is similar to the crushing and milling equipment of the previous group and has a rated capacity of 1,584 tons of milled cyanamide per 24 hours.

Liquid air group.—The liquid air plant, of a rated capacity of 12,800,000 cubic feet, or 300 tons of nitrogen, per 24 hours, is the largest liquid air installation in the world, and had a capacity when built greater than that of all other liquid air plants of the Western Hemisphere combined.

The air intakes are two 36-inch spiral riveted pipes extending, one north and one south, for 1,600 feet from a point near the north end of the building. The air is washed in eight sets of scrubbers of two to a set.

There are 15 compressors used in the air-liquifying process, 7 Ingersoll-Rand Co. twin duplex, 3-stage, displacement 1,186 c. f. m., discharge pressure 600 pounds, and 8 Norwalk Iron Works twin duplex, 3-stage compressors, of 1,364 c. f. m. displacement, and 600 pounds discharge pressure.

Each machine, after compressing the air to 450 pounds, delivers it through an after cooler and oil separator to one of the 30 nitrogen column equipments.

The nitrogen gas produced is delivered to the cyanamide ovens one-quarter of a mile to the west, through a 30-inch spiral riveted pipe.

This plant also contains an installation of five Sullivan vertical angle compound compressors, twin duplex, 2-stage, 2,016 c. f. m. capacity for compressed air (70 to 100 pounds) service throughout the plant.

Ammonia gas group.—The hydrating equipment of a rated capacity of 2,160 tons of hydrated cyanamide per 24 hours consists of three 36-inch by 36-foot hydrators in which the material is sprayed with water, agitated and discharged through screw conveyors to the autoclave building. The hydrators are 36-inch cut-flight conveyors with hoods attached for drawing off the resulting acetylene gas.

The silo building consists of nine 475-ton capacity concrete silos for storing unhydrated calcium cyanamide. The cyanamide as conveyed from the cyanamide mill can be fed either to the hydrator feeding bins direct or through these silos.

Steam for the autoclaves and for heating the plant buildings is supplied by the process steam plant of a total boiler capacity on 120 per cent rating of 3,950 horsepower.

Coal, dumped from railroad cars into a concrete track hopper, feeds through a 24 by 24 inch single-roll crusher to four 90-ton coal bunkers, from which it is fed through four measuring hoppers to four Westinghouse stokers, each serving a Babcock & Wilcox, Stirling type boiler of 823 horsepower.

The mechanical draft is furnished by four Sturtevant fans, each with a capacity of 26,000 c. f. m. The feed water, which is heated by a Cochrane feed-water heater, is delivered to the boilers by two 345 g. p. m. feed-water pumps. The ashes from the boilers are dumped into the ash-pit hopper, which feeds the skip serving an overhead-track hopper.

The autoclave building, with a rated capacity of 166⅔ tons of ammonia gas per 24 hours, contains 46 autoclaves, arranged in 14 rows of 4 each. These autoclaves, which are 6 feet diameter by 21 feet high, are constructed of welded steel plate of 1-inch thickness for the side walls and 1½ inches for the domed tops and bottoms, are fitted with an agitator which revolves at 11½ r. p. m. Each set of four autoclaves is operated by one 40-horsepower squirrel-cage induction motor.

The ammonia gas from the autoclaves is washed and dried by passing through a mud drum and an installation of columns and condensers.

There are seven ammonia columns, each 9 feet diameter by 19 feet high, connected by a 14-inch pipe to seven 7 feet 2 inch diameter by 8 feet 3 inch dephlegmators and seven condensers of the same size. The gas is collected from a point 21 inches above the bottom of each condenser and carried to two 60,000 cubic feet gas holders by a 20-inch diameter pipe.

The slurry from the autoclaves is piped to two filter buildings similarly equipped. Each building contains two steel slurry troughs, each of which feeds five vacuum filters 6 feet diameter by 3 feet, making one revolution in four and one-half minutes and having a capacity of 2½ tons of sludge per hour. The sludge from each set of five filters is conveyed to a sludge hopper, from which it is pumped by a 650 g. p. m. centrifugal pump to the dump. The filtrate is pumped from each set of ten filters by three 200 g. p. m. centrifugal pumps to eight open-top steel storage tanks 13 feet 6 inches diameter by 12 inches deep, from which it is pumped as needed by four centrifugal pumps into seven open-top steel tanks 6 feet diameter by 12 inches, called filtrate-measuring tanks.

The caustic equipment, for the preparation and distribution of the necessary caustic-soda solution, includes one lime-slaking tank, one liquid elevator, three reaction agitators equipped with air lifts and steam coils, three thickener tanks, three diaphragm pumps, one sludge tank, two 15 g. p. m. centrifugal pumps, one solution tank, and one 200 g. p. m. centrifugal solution pump.

Nitric acid group.—The six catalyzer buildings of this group contain equipment rated to oxidize sufficient ammonia gas to produce 280 tons of 100 per cent nitric acid per 24 hours.

Each catalyzer building contains four rows of catalyzer units, of which there are 29 catalyzers per row, or a total of 696 catalyzers for all six buildings. Each catalyzer unit consists of a rectangular aluminum tower 14 by 28 inches by 5 feet high, a pan near the bottom of the tower for holding the platinum gauze, an 80-mesh platinum gauze, 13 by 27 inches, woven of 0.003 inch diameter wire, and a cast-iron base on which the tower rests, all supported in a steel frame. The mixed gas passes through the top of the tower down over the heated platinum gauze and out the bottom through a brick flue to the coolers.

The ammonia gas is supplied from the gas holders through a 20-inch main, while air is furnished to all six buildings by two 300,000 c. f. m. blowers.

In the cooling and oxidation building there are 24 high-temperature coolers, 12 low-temperature coolers, and 12 oxidation towers. Only 12 high-temperature coolers are used at a time. The high-temperature coolers are 90 inches diameter by 12 feet long, horizontal, steel, tubular, marine-type boilers covered with an asbestos coating. The low-temperature coolers are 25 by 36 feet by 7 feet high, constructed of chemical brick, and have five passages so arranged that gas passes the full length of each cooler five times. Projecting down into each of these five passageways are 4 rows of 35 cooling tubes each (20 rows in all); the first 12 rows of tubes are made of duriron, and the last 8 rows are vitrified tubes. In each of these tubes is a galvanized-iron baffle cylinder which is supplied with water. The oxidation towers, which are of similar construction to the low-temperature coolers, except that they contain no cooling tubes, are 15 feet by 31 feet 6 inches by 15 feet high.

The absorption tower building, which is really a part of the cooling and oxidation building, houses 24 absorption towers 31 feet 6 inches by 34 feet 2 inches by 60 feet high. These towers are built of acid-proof masonry, with four compartments or chambers, each filled with 6-inch and 3-inch vitrified spiral tile, and are operated in pairs arranged in series. There is a 72-inch exhauster fan at the base of each tower to propel the gases through the tower. The acid is pumped over the towers by air lifts in acid wells, of which there are 120 in all, each 12 inches diameter by 96 feet deep. These wells have a steel casing, while the piping carrying the acid is of aluminum and duriron.

For weighing the acid there are twelve 11 feet diameter by 10 feet aluminum tanks, each equipped with a Fairbanks beam scale. There are also 12 closed storage tanks of a total capacity of 3,500 tons of 40 per cent acid solution, each 31 feet diameter by 10 feet high, constructed of reinforced concrete, lined with chemical brick.

Ammonium nitrate group.—The neutralizer equipment of a rated capacity of 600 tons of 50 per cent solution of ammonium nitrate per 24 hours is composed of four units, each consisting of an aborption tower 6 feet 6 inches square by 30 feet high, of acid brick, and comprising one chamber filled with vitrified spiral tile; one cooler or condenser, 7 feet 6 inches by 13 feet by 8 feet high, constructed like the low-temperature coolers of the nitric-acid equipment; one neutralizer tank, 11 by 26 feet by 7 feet high, of chemical brick; one 11 feet diameter by 10 feet acid supply tank, of chemical brick, supplying two neutralizer units; four settling tanks, each 18 feet diameter by 6 feet and acid brick lined; three Sperry filter presses; one 18 feet diameter by 6 feet filtrate tank; and a system of five acid wells serving two neutralizing units.

From this plant the liquor is pumped to eight 20 feet diameter by 18 feet steel storage tanks by five 200 g. p. m. centrifugal pumps, and from these tanks to the 12 feet diameter by 12 feet tanks outside of each of the ammonium nitrate buildings by two 200 g. p. m. centrifugal pumps.

There are five similar ammonium nitrate houses, each equiped with ten 6 feet 6 inches by 11 feet enameled evaporating pans, and twenty 5 feet diameter by 18 inches crystalizing pans and grainers. Above each evaporating pan is a sheet steel hood for drawing off steam.

Shops group.—The machine shop includes, besides the machine equipment, a tool room, an office, and an engine repair shop with 3 floor pits, and is equipped with 2 bolt-threading machines, 4 bending machines, 3 cutters, 12 drill presses of various sizes, 8 grinders, 6 power hack saws, 8 lathes, 2 milling machines, 2 punch and shear machines, 3 pipe cutting and threading machines, a 200-ton hydraulic press, a planer, a riveting machine, 2 shapers, 3 shearing machines, a tool grinder, and miscellaneous smaller equipment.

The foundry building is equipped with a 44-inch cupola, with the necessary riddle, sand blast, sand mixer, grinders, core ovens, etc.

The blacksmith shop contains nine forges, pressure blower, exhaust fan, grinders, shears, and one 50-pound and one 1,100-pound hammer.

The woodworking shop is completely equipped with lathes, planers, surfacers, power saws, mortise and tenoning machines, sanders, boring machines, and smaller equipment.

Power group.—The power required, approximately 90,000 kilowatts, is furnished, 60,000 kilowatts by the river power house on the reservation and 30,000 kilowatts by the Government addition to the Warrior River station of the Alabama Power Co., 89 miles distant.

The main equipment of the large generating station, which is of concrete substructure, structural steel frame with brick walls, and tile roof, consists of 12 B. & W. Stirling type boilers each of 1,507 nominal boiler horsepower, equipped with Westinghouse underfeed stokers, each of 284 square feet grate surface, and Green fuel economizer forced-draft fans of a capacity of 50,000 cubic feet per minute. There are three chimneys, two 275 feet high by 14 feet inside diameter at top, each serving three boilers; and one 275 feet high by 18 feet inside diameter at top serving six boilers. The four 5-inch centrifugal boiler feed pumps, two 15,000-horsepower Cochrane feedwater heaters, four circulating pumps each 3-stage centrifugal pumps of 44,000 g. p. m. capacity, and four Westinghouse surface condensers, each having a tube surface of 25,000 square feet, complete the principal equipment of the steam generating end.

In the electrical generating section there is the 60,000-kilowatt Westinghouse Parsons double-flow type cross-compound turbine in three elements—one high pressure at 1,800 r. p. m. exhausting into two low-pressure elements at 1,200 r. p. m., each direct connected to a 23,000 kv.-a., 12,200 volts, 3-phase, 60-cycle Westinghouse generator. Then there are two "house" turbines, each direct connected to a 2,500 kv.-a., 2,300-volt, 3-phase generator; two turbo exciters, and four motor exciters.

The power generated is carried to the plant through copper bus bars in a tunnel of concrete and tile construction.

The 30,000-kilowatt extension at Gorgas, Ala., on the Black Warrior River, consists primarily of one 30,000-kilowatt General Electric Co. (33,333 kv.-a.) 13,200-volt, 3-phase, 60-cycle turbo generator, with 140-kilowatt, 250-volt, direct-connected, direct-current exciter; twelve 1,200-horsepower B. & W. Stirling type boilers, with superheaters of 225 pounds pressure and 200° F., equipped with eleven 12-retort Westinghouse underfeed stokers and one 12-retort Taylor stoker, and one 56,000 square foot Worthington surface condenser.

The station is of structural steel and brick construction, and is served by one 225 feet by 18 feet, inside diameter, radial brick stack.

The power generated is delivered to the plant over a transmission line consisting of three 250,000 c. m. (B. & S. gauge) copper conductors supported by suspension-type insulators from H-frame structures consisting of two creosoted wooden poles and wooden cross arms.

Quarry group.—For the supply of process limestone, a limestone quarry was opened and a crusher plant erected near Russellville, Ala., 30 miles south of the plant, and known as Waco quarry.

The main equipment of the crushing plant consists of a set of Edison rolls, 60 by 48 inches, and one Traylor 26-inch gyratory crusher as the primary crushing plant, and a secondary one of two Gates No. 6 gyratory crushers. Storage bins of but two days' capacity were provided because of the large available storage at the nitrate plant.

Miscellaneous.—There is installed in the manufacturing area some 26 miles of process piping of sizes one-fourth inch to 30 inches, 27 miles of 4-inch fiber conduit, 3 miles of concrete conduit, and 20 miles of cable. For driving the various pieces of equipment there are installed 608 electric motors of a total connected capacity of 21,003 horsepower.

The buildings of this area are all of concrete substructure, with structural steel frame superstructure, walled in with either corrugated iron or interlocking tile, and having concrete slab and slag roofs. These structures cover some 29 acres of ground space.

The carbide furnace and electrode repair building, 90 by 1,050 feet in plan by 64 feet to top of monitor, if placed over the Union Station, Washington, D. C., would entirely hide it; the cyanamide oven building is 250 by 520 feet in plan by 62 feet 6 inches to top of monitor; the liquid air building 100 by 575 feet in plan by 52 feet 6 inches high; and the cooling and absorption building 200 by 600 feet in plan by 90 feet 6 inches high, has a ground area 10 per cent in excess of the ground area of the United States Capitol building.

For the housing of the permanent plant operating force an industrial village was erected throughout the western half of the reservation. This village, although not completed according to original plans because of the signing of the armistice, consists of 186 houses of two to seven rooms, one and two story, frame construction; stucco, shingle, or clapboard exteriors; concrete or hollow-tile foundation; and an administration quarters of 100 rooms, one-story frame construction, shingle exterior, slate roof, and concrete foundation. In addition there is a negro village of 263 houses of 3 rooms and 10 apartment houses, all of one-story frame construction covered with tar paper.

Auxiliary to the plant and village there is installed a domestic water and fire system 16 miles in length, together with a raw water reservoir of 60,000,000-gallon capacity, a settling basin of 300,000-gallon capacity, a filter plant of 1,500,000 gallons per 24 hours capacity, a clear-water basin of 500,000-gallon capacity, a reservoir-pumping station of 44,420 g. p. m., and a process-water system throughout the chemical plant 3 miles in length; a 20-mile sanitary sewer system; and a sewage-disposal plant consisting of a 300,000-gallon capacity Imhoff tank, sludge bed, and chlorinator plant.

There have been constructed throughout the reservation 22.18 miles of roads of slag with a chert binder, oiled with Tarvia B, and covered with a light coat of limestone screenings. Of the 49.8 miles of railroad track laid, 37.1 miles now remain as the permanent plant railroad system trackage.

Ice for village purposes is produced in an ice and refrigerating plant of 50-tons per day capacity. This building is a one-story brick structure with slate roof and concrete foundations.

APPENDIX C.

ESTIMATE OF PRODUCTION COSTS, UNITED STATES NITRATE PLANT NO. 2.

These estimates were prepared in the summer of 1919 to show the estimated cost of manufacturing commercially cyanamide, sulphate of ammonia, and nitrate of ammonia in United States Nitrate Plant No. 2 under the scheme of operation then proposed. These estimates applied to the operation of 8 of the 10 regularly operating carbide furnaces and corresponding equipment for the production of lime nitrogen or crude cyanamide. One-fourth of the lime nitrogen produced was to have been oiled and hydrated to produce 49,000 tons of commercial cyanamide per year, one-fourth used to make 22,000 tons of nitrate of ammonia per year, and one-half to make 86,000 tons of sulphate of ammonia per year. Operation of the plant at full instead of 80 per cent capacity would undoubtedly result in some saving over the costs shown here.

Five main items—production cost, bagging, sales, research and main office, and royalties and fees—enter into the final cost of these products f. o. b. cars Muscle Shoals, Ala.

In the production cost estimates the quantity of raw materials and power used in the manufacture of the several products was based on the actual results of the two weeks' operating test of the plant at one-fifth capacity in January, 1919. The quantity of materials used in the several manufacturing processes were carefully measured and weighed daily and the consumption for the entire period of the test thus determined. The quantity of products manufactured were also carefully determined.

The unit prices of materials and rates of labor are those which existed at the time the estimate was made, the summer of 1919, and it is believed are not very different from those that will prevail in the future as conditions become more stabilized.

The cost estimated for steam power is the estimated generating expense under the conditions assumed in the estimate. The cost for water power is a figure applicable only to the particular circumstances applying to the proposed scheme of operation and is considerably lower than the usual commercial cost.

The items for repairs and maintenance were estimated on the basis of total yearly expense, and this amount, $488,134 for labor and $259,527 for material, or $747,661 total, was prorated over the several products. This allowance, based upon experience in similar plants, is believed to be liberal.

A detailed labor-organization sheet was prepared, giving the number of men necessary, together with their rates of pay, for the operation, maintenance, and supervision of every part of the plant, and is included in this estimate. Ten per cent for contingencies was added to all labor items.

In estimating bagging expense it was assumed that all the commercial cyanamide and all the nitrate of ammonia must be bagged, but that two-thirds of the sulphate of ammonia would be shipped in bulk.

Sales expense was estimated at 3½ per cent of the cost of the material f. o. b. Muscle Shoals.

Research and main office expense was estimated at $235,000 per year and prorated according to cost of products.

Expense for royalties and fees was figured in accordance with the provisions of existing contracts with the American Cyanamid Co. and its subsidiary, the Air Nitrates Corporation, and with the Air Reduction Co., due consideration being given to arbitration clauses.

These estimates do not include any allowance for interest on capital cost, depreciation and obsolescence, or taxes and insurance. They were also based upon the assumption that all community arrangements would be self-supporting in so far as current operating expenses were concerned.

Estimated cost of final products.

	Commercial cyanamide.	Nitrate of ammonia.	Sulphate of ammonia.
Steam power costs:			
Production cost, using steam power	$29.02	$80.48	$49.45
Bagging and loading	1.75	2.00	[1] .50
Sales	1.15	3.08	1.87
Research and main office	.95	2.55	1.54
Cost without royalties, using steam power	32.87	88.11	53.36
Allowance for royalties at 10 per cent, assuming reduction by arbitration	3.29	8.81	5.34
Cost f. o. b. cars Muscle Shoals, using steam power	36.16	96.92	58.70
Water power costs (after completion of Wilson Dam):			
Production cost, using water power	20.72	60.78	39.79
Bagging	1.75	2.00	.50
Sales	1.15	3.08	1.87
Research and main office	.95	2.55	1.54
Cost without royalties, using water power	24.57	68.41	43.70
Allowance for royalties at 10 per cent, assuming reduction by arbitration	2.46	6.84	4.37
Cost f. o. b. cars Muscle Shoals, using water power	27.03	75.25	48.07

[1] Average for entire output; estimated less than 35 per cent of product will be bagged.

Detailed estimates of production costs.

ESTIMATED PRODUCTION COST OF CRUDE CALCIUM CYANAMIDE.

Item.	Quantity per ton of cyanamide.	Unit cost.	Cost per ton of crude calcium cyanamide.	
			Using steam power.	Using water power.
Limestone	1.75 tons	$1.25	$2.19	$2.19
Coke	0.54 tons	6.00	3.24	3.24
Coal	0.21 tons	4.00	.84	.84
Electrodes	37.8 pounds	.05	1.89	1.89
Steam power	2,808 kilowatt-hours	.004	11.23	
Water power	do	.00075		2.10
(Charcoal and diluent			.59	.59
Caustic soda			.13	.13
Miscellaneous materials)			.86	.86
Repair parts			1.08	1.08
Labor (operation)			5.09	5.09
Labor (maintenance)			2.11	2.11
Superintendence			1.58	1.58
Fire department			.27	.27
Total			31.10	21.97

ESTIMATED PRODUCTION COST OF COMMERCIAL CYANAMID.

One ton of crude cyanamide, when oiled and hydrated, produces approximately 1.10 tons commercial cyanamid, at an estimated cost of $0.75 per ton for oil and oiling.

$31.10÷1.10	$28.27
Oil and oiling	.75
Production cost of commercial cyanamid using steam power	29.02
$21.97÷1.10	19.97
Oil and oiling	.75
Production cost of commercial cyanamid using water power	20.72

ESTIMATED PRODUCTION COST OF AMMONIA GAS.

Item.	Quantity per ton of ammonia gas.	Unit cost.	Cost per ton ammonia gas.	
			Using steam power.	Using water power.
Crude cyanamide	4.025 tons	$31.10	$125.18	
Do	do	21.97		$88.43
Steam power	130 kilowatt-hours	.004	.52	
Water power	do	.00075		.10
Soda ash	0.134 tons	25.00	3.35	3.35
Steam	8 M pounds	.285	2.28	2.28
Compressed air	2.7 M cubic feet	.013	.04	.04
Miscellaneous supplies and repair parts			.75	.75
Labor (operation)			4.06	4.06
Labor (maintenance)			.70	.70
Additional superintendence			.42	.42
Total			137.30	100.13

NOTE.—Crude cyanamide when produced by steam power costs $31.10 per ton, by water power $21.97.

ESTIMATED PRODUCTION COST OF SULPHATE OF AMMONIA.

Item.	Quantity per ton of sulphate.	Unit cost.	Cost per ton sulphate.	
			Using steam power.	Using water power.
Ammonia gas	0.257 tons	$137.30	$35.28	
Do	do	100.13		$25.73
Steam power	35 kilowatt-hours	.004	.14	
Water power	do	.00075		.03
Sulphuric acid, 60°	0.96 ton	10.00	9.60	9.60
Coal, steam, air			.11	.11
Miscellaneous supplies and repair parts			.70	.70
Labor (operation)			2.77	2.77
Labor (maintenance)			.57	.57
Additional superintendence			.28	.28
Total			49.45	39.79

NOTE.—Ammonia gas produced by steam power costs $137.30 per ton; by water power, $100.13.

ESTIMATED PRODUCTION COST OF NITRIC ACID (COMPUTED ON BASIS OF 100 PER CENT ACID.)

Item.	Quantity per ton of nitric acid.	Unit cost.	Cost per ton nitric acid.	
			Using steam power.	Using water power.
Ammonia gas	0.317 tons	$137.30	$43.52	
Do	do	100.13		$31.74
Steam power	344 kilowatt-hours	.004	1.37	
Water power	do	.00075		.25
Compressed air	42.37 M cubic feet	.013	.55	.55
Miscellaneous supplies and repair parts			1.95	1.95
Labor (operation)			2.02	2.02
Labor (maintenance)			1.23	1.23
Additional superintendence			.24	.24
Total			50.88	37.98

NOTE.—Ammonia gas produced by steam power costs $137.30 per ton; by water power $100.13.

ESTIMATED PRODUCTION COST OF NITRATE OF AMMONIA.

Item.	Quantity per ton of nitrate.	Unit cost.	Cost per ton nitrate.	
			Using steam power.	Using water power.
Nitric acid	0.858 ton	$50.88	$43.66	
Do	do	37.98		$32.59
Ammonia gas	0.230 ton	137.30	31.58	
Do	do	100.13		23.03
Steam power	25 kilowatt-hours	.004	.10	
Water power	do	.00075		.02
Compressed air	14.33 M cubic feet	.013	.19	.19
Steam	1.86 M pounds	.285	.53	.53
Miscellaneous supplies and repair parts			.60	.60
Labor (operation)			2.61	2.61
Labor (maintenance)			.80	.80
Additional superintendence			.41	.41
Total			80.48	60.78

NOTE.—Nitric acid when made from ammonia produced by steam power cost $50.88 per ton; by water power, $37.98. Ammonia gas produced by steam power cost $137.30; by water power, $100,13.

Royalties and fees.

	Royalty to		Total per ton.
	Air Reduction Co.	American Cyanamid Co.	
Commercial cyanamide	[1] $0.522	[2] $5.753	$6.275
Nitrate of ammonia	[1] 1.16	[2] 10.395	11.555
Sulphate of ammonia	[1] .594	[2] 6.176	6.770

[1] Royalty to Air Reduction Co. until January, 1931, is $2.72 per ton of nitrogen fixed as lime nitrogen after that date there will be no royalty charge.

[2] Royalty to American Cyanamid Co. is $30 per ton of nitrogen content in any and all products manufactured, the figure $30, however, being subject to arbitration.

Details of labor—Summary of pay roll.

	Number of men.	Yearly pay roll.
Operating force	840	$1,249,103
Maintenance force	244	438,070
Superintendence	184	282,700
Total	1,268	1,969,873
10 per cent added for contingencies	127	196,987
Grand total	1,395	2,166,860

NOTE.—In addition to the force shown above, 141 men will be employed in general utilities—steam electric power, process steam and compressed air. The pay roll for these men amounts to $228,267 per year, and this appears in the detailed estimates of production costs as a part of the cost of steam power, process steam, and compressed air. This brings the force up to 1,536. This total does not include men engaged in bagging and loading, or those engaged in self-supporting community activities.

Operating force—Summary of pay rolls by departments.

	Number of men.	Daily pay roll.
Cyanamide:		
Coke mill	10⅔	$46.43
Coal mill	10⅔	59.43
Limekiln	23⅔	101.63
Raw materials and yard	39	156.10
Raw materials building	6	16.80
Carbide furnace	233	911.60
Electrode shop	19	85.47
Carbide mill	46	176.49
Liquid air	62	283.47
Cyanamide oven room	64	250.00
Cyanamide mill and cooling shed	43	168.10
Total	560	[1] 2,255.52
Ammonia gas:		
Hydrating building	6.8	30.72
Autoclaves	64.2	247.65
Filter building	15	56.40
Total	86	[1] 334.77
Sulphate of ammonia:		
Total force	140	[1] 593.17
Nitric acid:		
Total force	20	[1] 95.68
Nitrate of ammonia:		
Neutralizer section	12½	54.74
Nitrate section	21½	88.34
Total	34	[1] 143.08
Grand total	840	3,422.22

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[1] In carrying this amount forward to detailed estimates of production cost, 10 per cent has been added to cover contingencies, etc.

Detailed pay roll.

CRUDE CYANAMIDE.

Rating.	No.	Daily pay roll.
Coke mill:		
Superintendent, $300 per month	⅓	$3.33
Clerk, $135 per month	⅓	1.50
Shift foreman, $180 per month	1	6.00
Dryer operators, $0.55 per hour	3	13.20
Crusher operators, $0.525 per hour	2	8.40
Conveyor operators, $0.525 per hour	2	8.40
Laborers, $0.35 per hour	2	5.60
Total	10⅔	46.43
Coal mill:		
Superintendent, $300 per month	⅓	3.33
Clerk, $1 5 per month	⅓	1.50
Shift foreman, $180 per month	1	6.00
Dryer operators, $0.55 per hour	3	13.20
Pulverizer operators, $0.60 per hour	3	14.40
Conveyor operators, $0.525 per hour	3	12.60
Laborers, $0.35 per hour	3	8.40
Total	13⅔	59.43
Lime kiln:		
Superintendent, $300 per month	⅓	3.33
Clerk, $135 per month	⅓	1.50
Shift foreman, $180 per month	1	6.00
Kiln operators, $0.65 per hour	9	46.00
Conveyor operators, $0.525 per hour	6	25.20
Laborers, $0.35 per hour	7	19.60
Total	25⅔	101.65

Detailed pay roll—Continued.

CRUDE CYANAMIDE—Continued.

Rating.	No.	Daily pay roll.
Raw materials and yard:		
Yard foreman, $195 per month	1	$6.50
Locomotive engineers, $6 per day	2	12.00
Locomotive firemen, $4.40 per day	2	8.80
Brakemen, $4.40 per day	2	8.80
Conductors, $6 per day	2	12.00
Crane engineers, $6 per day	5	30.00
Crane firemen, $4.40 per day	5	22.00
Laborers, $0.35 per hour	20	56.00
Total	39	156.10
Raw-material building:		
Laborers, $0.35 per hour	6	16.80
Total	6	16.80
Carbide furnace room:		
Superintendent, $300 per month	1	10.00
Shift foremen, $200 per month	3	20.00
Clerk, $150 per month	1	5.00
Furnace men (first class), $0.625 per hour	9	45.00
Furnace men (second class), $0.45 per hour	120	432.00
Tappers (first class), $0.625 per hour	24	120.00
Tappers (second class), $0.45 per hour	24	86.40
Locomotive drivers, $0.525 per hour	9	37.80
Locomotive helpers, $0.525 per hour	6	25.20
Cranemen, $0.525 per hour	3	12.60
Belt men, $0.55 per hour	3	13.20
Belt-men helpers, $0.45 per hour	6	21.60
Weighers, $0.525 per hour	6	25.20
Weighers' helpers, $0.45 per hour	9	32.40
Laborers, $0.35 per hour	9	25.20
Total	233	911.60
Electrode shop:		
Foreman, $200 per month	1	6.67
Drillers, $0.55 per hour	2	8.80
Planers, $0.55 per hour	2	8.80
Pipe fitters, $0.875 per hour	3	21.00
Assemblers, $0.55 per hour	3	13.20
Assembler helpers, $0.45 per hour	4	14.40
Cranemen, $0.525 per hour	1	4.20
Laborers, $0.35 per hour	3	8.40
Total	19	85.47
Carbide mill:		
Superintendent, $300 per month	½	5.00
Shift foremen, $190 per month	3	18.99
Clerks, $150 per month	½	2.50
Crusher operator, $0.525 per hour	3	12.60
Hardinge mill operators, $0.525 per hour	3	12.60
Smidth mill operators, $0.525 per hour	3	12.60
Smidth mill helpers, $0.425 per hour	3	10.20
Conveyor operators, $0.525 per hour	3	12.60
Locomotive drivers, $0.40 per hour	3	9.60
Crane operators, $0.525 per hour	3	12.60
Chill car operators, $0.40 per hour	6	19.20
Laborers, $0.40 per hour	15	48.00
Total	46	176.49
Liquid air:		
Superintendent, $350 per month	1	11.67
Clerk, $135 per month	1	4.50
Shift foremen, $7.50 per day	3	22.50
Column operators, $0.55 per hour	36	158.40
Compressor operators, $0.55 per hour	9	39.60
Soda tower operators, $0.525 per hour	6	25.20
Switchboard operators, $0.55 per hour	3	13.20
Laborers, $0.35 per hour	3	8.40
Total	62	283.47

Detailed pay roll—Continued.

CRUDE CYANAMIDE—Continued.

Rating.	No.	Daily pay roll.
Cyanamide oven room:		
Superintendent, $300 per month	1	$10.00
Shift foremen, $200 per month	3	20.00
Clerk, $150 per month	1	5.00
Head paper man, $0.45 per hour	1	3.60
Paper men, $0.35 per hour	4	11.60
Chargers, $0.625 per hour	6	30.00
Dischargers, $0.55 per hour	3	13.20
Crane men, $0.525 per hour	9	37.80
Conveyor men, $0.45 per hour	3	10.80
Oven attendants, $0.40 per hour	21	67.20
Pencil men, $0.50 per hour	6	24.00
Laborers, $0.35 per hour	6	16.80
Total	64	250.00
Cyanamide mill and cooling shed:		
Superintendent, $300 per month	½	5.00
Shift foremen, $190 per month	3	19.00
Clerk, $150 per month	½	2.50
Crane men, $0.525 per hour	6	25.20
Crane men helpers, $0.40 per hour	6	19.20
Crusher operators, $0.525 per hour	3	12.60
Hardinge mill operators, $0.525 per hour	3	12.60
Smidth mill operators, $0.525 per hour	3	12.60
Conveyor men, $0.525 per hour	3	12.60
Crane men, $0.45 per hour	6	21.60
Laborers, $0.35 per hour	9	25.20
Total	43	168.10
Grand total	560	2,255.52

NOTE.—The above totals are carried over to summary without adding 10 per cent for contingencies, etc.

AMMONIA GAS.

Hydrating building:		
Superintendent, $300 per month	0.1	$1.00
Shift foreman, $200 per month	.3	2.00
Clerk, $125 per month	.1	.42
Chief operators, $0.625 per hour	.3	1.50
Operators, $0.55 per hour	3	13.20
Conveyor man, $0.525 per hour	3	12.60
Total	6.8	30.72
Autoclaves:		
Superintendent, $300 per month	.9	9.00
Shift foremen, $200 per month	2.7	18.00
Clerk, $125 per month	.9	3.75
Chief operators, $0.625 per hour	2.7	13.50
Top operators, $0.55 per hour	12	52.80
Top operator helpers, $0.50 per hour	12	48.00
Bottom operator, $0.45 per hour	6	21.60
Bottom operator helpers, $0.40 per hour	6	19.20
Weigher, $0.45 per hour	12	32.40
Conveyor men, $0.525 per hour	3	12.60
Laborers, $0.35 per hour	6	16.80
Total	64.2	247.65

Detailed pay roll—Continued.

AMMONIA GAS—Continued.

Rating.	No.	Daily pay roll.
Filter building:		
Operators, $0.55 per hour	3	$13.20
Operator helpers, $0.45 per hour	6	21.60
Pump men, $0.55 per hour	3	13.20
Laborers, $0.35 per hour	3	8.40
Total	15	56.40
Grand total	86	334.77

NOTE.—The above totals are carried over to summary without adding 10 per cent for contingencies, etc.

SULPHATE OF AMMONIA.

Superintendent, $300 per month	1	$10.00
Foremen, $180 per month	3	18.00
Clerk, $125 per month	1	4.17
Centrifugal men, $0.5625 per hour	42	189.00
Centrifugal helpers, $0.50 per hour	42	168.00
Absorber men, $0.625 per hour	12	60.00
Absorber helpers, $0.50 per hour	12	48.00
Drier men, $0.5625 per hour	12	54.00
Laborers, $0.35 per hour	15	42.00
Total	140	593.17

NOTE.—The above totals are carried over to summary without adding 10 per cent for contingencies, etc

NITRIC ACID.

Superintendent, $300 per month	½	$5.00
Foreman, $200 per month	3	20.00
Clerk, $125 per month	½	2.08
Platinum repair man, $150 per month	1	5.00
Chief operator, $150 per month	3	15.00
Tower men, $150 per month	3	15.00
Operators, $0.50 per hour	3	12.00
Tower men helpers, $0.45 per hour	6	21.60
Total	20	95.68

NOTE.—The above totals are carried over to summary without adding 10 per cent for contingencies, etc.

NITRATE OF AMMONIA.

Neutralizer section:		
Superintendent, $300 per month	¼	$2.50
Clerk, $125 per month	¼	1.04
Shift foremen, $200 per month	3	20.00
Operators, $0.50 per hour	3	12.00
Operator helpers, $0.45 per hour	3	10.80
Laborers, $0.35 per hour	3	8.40
Total	12½	54.74
Nitrate section:		
Superintendent, $300 per month	¼	2.50
Clerk, $125 per month	¼	1.04
Shift foremen, $200 per month	3	20.00
Evaporator operators, $0.55 per hour	3	13.20
Grainer operators, $0.55 per hour	3	13.20
Operator helpers, $0.45 per hour	6	21.60
Laborers, $0.35 per hour	6	16.80
Total	21½	88.34
Grand total	34	143.08

NOTE.—The above totals are carried over to summary without adding 10 per cent for contingencies, etc.

Maintenance force.

Rating.	Rate of pay.	No.	Daily pay roll.	Charged to—									
				Crude cyanamide.		Ammonia gas.		Sulphate of ammonia.		Nitric acid.		Nitrate of ammonia.	
				No.	Daily pay roll.	No.	Daily pay roll.	No.	Daily pay roll.	No.	Daily pay roll.	No.	Daily pay roll.
Mechanical superintendent	$5,000.00	1	$13.70	1	$13.70								
Master mechanic	3,600.00	1	9.90	1	9.90								
Chief electrician	3,600.00	1	9.90	1	9.90								
Draftsmen	1,500.00	5	20.63	5	20.63								
Clerks	1,500.00	4	16.42	4	16.42								
Stenographers	1,200.00	2	6.67	2	6.67								
Foreman, machinist	2,000.00	1	5.50	1	5.50								
Foreman, pipefitter	2,000,00	1	5.50	1	5.50								
Foreman, carpenter	2,000.00	1	5.50	1	5.50								
Foremen, electrician	2,000.00	2	11.00	2	11.00								
Foreman, labor	2,000.00	1	5.50	1	5.50								
Machinists	p.d.6.00	13	78.00	12	72.00			1	$6.00				
Pipefitters	p.d.7.00	10	70.00	9	63.00			1	7.00				
Steamfitters	p.d.7.00	6	42.00			2	$14.00			2	$14.00	2	$14.00
Steamfitters' helpers	p.d.3.60	6	21.60			2	7.20			2	7.20	2	7.20
Plumbers	p.d.7.00	2	14.00	2	14.00								
Carpenters	p.d.5.00	15	75.00	11	55.00			4	20.00				
Blacksmiths	p.d.5.60	2	11.20	2	11.20								
Blacksmiths' helpers	p.d.3.60	4	14.40	4	14.40								
Tinsmiths	p.d.7.00	4	28.00	4	28.00								
Painters	p.d.6.00	5	30.00	4	24.00			1	6.00				
Masons	p.d.7.00	9	63.00	7	49.00			1	7.00	1	7.00		
Masons' helpers	p.d.3.60	1	3.60							1	3.60		
Electricians	p.d.6.00	30	180.00	24	144.00	1	6.00	1	6.00	3	18.00	1	6.00
Millwrights	p.d.4.80	33	158.40	24	115.20	3	14.40	4	19.20			2	9.60
Millwright helpers	p.d.3.60	33	118.80	24	86.40	3	10.80	4	14.40			2	7.20
Welders	p.d.7.00	3	21.00	3	21.00								
Riggers	p.d.7.00	3	21.00	3	21.00								
Lead burners	p.d.8.00	2	16.00					2	16.00				
Lead burners' helpers	p.d.3.60	2	7.20					2	7.20				
Filter recoverer	p.d.4.80	1	4.80			1	4.80						
Laborers	p.d.2.80	40	112.00	32	89.60			5	14.00	3	8.40		
Total		244	1,200.22	185	918.02	12	57.20	26	122.80	12	58.20	9	44.00

The above does not include the 10 per cent allowance for contingencies, etc., which is added to all labor items which appear in the detailed estimates of production cost.

Superintendence.

Rating.	Salary per year.	No.	Yearly pay roll.	Charged to—									
				Crude cyanamide.		Ammonia gas.		Sulphate of ammonia.		Nitric acid.		Nitrate of ammonia.	
				No.	Yearly pay roll.	No.	Yearly pay roll.	No.	Yearly pay roll.	No.	Yearly pay roll.	No.	Yearly pay roll.
General office and supervisory force:													
Works manager	$7,500	1	$7,500	1	$7,500								
Assistant to works manager	2,400	3	7,200	2	4,800			1	$2,400				
Paymaster	2,400	1	2,400	1	2,400								
Purchasing agent	3,600	1	3,600	1	3,600								
Assistant purchasing agent	2,700	1	2,700	1	2,700								
Accountants	2,000	4	8,000	3	6,000			1	2,000				
General superintendent	5,000	1	5,000	1	5,000								
Assistant general superintendent	3,000	1	3,000	1	3,000								

Superintendence—Continued.

Rating.	Salary per year.	No.	Yearly pay roll.	Charged to—									
				Crude cyanamide.		Ammonia gas.		Sulphate of ammonia.		Nitric acid.		Nitrate of ammonia.	
				No.	Yearly pay roll.	No.	Yearly pay roll.	No.	Yearly pay roll.	No.	Yearly pay roll.	No.	Yearly pay roll.
General office and supervisory forces:													
Technical assistant	$2,500	1	$2,500	1	$2,500	....	....	....	....	....	....	....	....
Do	1,800	2	3,600	2	3,600	....	....	....	....	....	....	....	....
Draftsmen	1,800	2	3,600	2	3,600	....	....	....	....	....	....	....	....
Clerks, special	1,800	8	14,400	8	14,400	....	....	....	....	....	....	....	....
Clerks	1,500	19	28,500	16	24,000	2	$3,000	1	$1,500	....	....	....	....
Do	1,400	14	19,600	9	12,600	2	2,800	1	1,400	1	$1,400	1	$1,400
Do	1,200	8	9,600	7	8,400	....	....	1	1,200	....	....	....	....
Stenographers	1,400	12	16,800	9	12,600	1	1,400	1	1,400	....	....	1	1,400
Typists	1,200	10	12,000	7	8,400	1	1,200	1	1,200	....	....	1	1,200
Telephone operators	900	4	3,600	4	3,600	....	....	....	....	....	....	....	....
Timekeepers	1,200	18	21,600	13	15,600	1	1,200	2	2,400	1	1,200	1	1,200
Janitors	800	3	2,400	3	2,400	....	....	....	....	....	....	....	....
Messengers and office boys	400	6	2,400	6	2,400	....	....	....	....	....	....	....	....
Total	....	120	180,000	98	149,100	7	9,600	9	13,500	2	2,600	4	5,200
Chemical laboratory force:													
Chief chemist	4,000	1	4,000	1	4,000	....	....	....	....	....	....	....	....
Chemists	2,400	7	16,800	6	14,400	....	....	1	2,400	....	....	....	....
Analysts	1,500	34	51,000	25	37,500	2	3,000	4	6,000	1	1,500	2	3,000
Typists	1,200	2	2,400	2	2,400	....	....	....	....	....	....	....	....
Clerk	1,500	1	1,500	1	1,500	....	....	....	....	....	....	....	....
Total	....	45	75,700	35	59,800	2	3,000	5	8,400	1	1,500	2	3,000
First aid:													
Doctor	2,800	1	2,800	1	2,800	....	....	....	....	....	....	....	....
Nurses	1,400	3	4,200	3	4,200	....	....	....	....	....	....	....	....
Total	....	4	7,000	4	7,000	....	....	....	....	....	....	....	....
Transportation force:													
Transportation foreman	2,200	1	2,200	1	2,200	....	....	....	....	....	....	....	....
Motor mechanics	1,800	1	1,800	1	1,800	....	....	....	....	....	....	....	....
Chauffeurs	1,000	6	6,000	6	6,000	....	....	....	....	....	....	....	....
Total	....	8	10,000	8	10,000	....	....	....	....	....	....	....	....
Water and sewage force:													
Foreman	2,800	1	2,800	1	2,800	....	....	....	....	....	....	....	....
Operators	1,200	6	7,200	6	7,200	....	....	....	....	....	....	....	....
Total	....	7	10,000	7	10,000	....	....	....	....	....	....	....	....
Total	....	184	282,700	152	235,900	9	12,600	14	21,900	3	4,100	6	8,200
Total, plus 10 per cent for contingencies, etc	....	....	310,970	....	259,490	....	13,860	....	24,090	....	4,510	....	9,020
Supplies:													
Office	....	....	9,000	....	9,000	....	....	....	....	....	....	....	....
Laboratory	....	....	7,500	....	7,500	....	....	....	....	....	....	....	....
First aid	....	....	1,000	....	1,000	....	....	....	....	....	....	....	....
Transportation	....	....	2,000	....	2,000	....	....	....	....	....	....	....	....
Water and sewage	....	....	2,000	....	2,000	....	....	....	....	....	....	....	....
Total	....	....	21,500	....	21,500	....	....	....	....	....	....	....	....
Grand total	....	....	332,470	....	280,990	....	13,860	....	24,090	....	4,510	....	9,020

NOTE.—In some cases the salary given is the average for the several employees of the same designation.

BIBLIOGRAPHY.

This bibliography is a list of pertinent references covering the period from the present to and including the year 1917. References previous to this may be found in Literature of the Nitrogen Industry, 1912–1916, J. Ind. & Eng. Chem. 424, vol. 9, No. 4 (1917).

These references are arranged in the order of the chapter of this report to which they refer.

CHAPTER II. UTILIZATION AND SOURCES OF NITROGEN.

II–A–Utilization.

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